REGISTERED NO. M. 3121

PROCEEDINGS

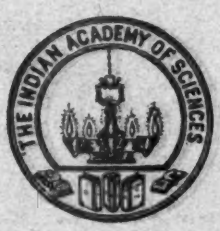
OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. VI] *SECTION A* [NO. 2

AUGUST, 1937



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PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, HEBBAL, BANGALORE.

NOTICE

The nineteenth Scientific Meeting of the Academy will be held on Saturday, 4th September 1937, at 5-15 p.m., in the Central Building of the Indian Institute of Science, Bangalore.

Papers Communicated for the Nineteenth Scientific Meeting of the Academy to be held on Saturday, the 4th September 1937, at 5-15 P.M., in the Central Building of the Indian Institute of Science, Bangalore

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THE RAMAN SPECTRA OF *DEXTRO*, *LAEVO* AND RACEMIC FORMS OF BORNEOL AND CAMPHOR.

By Baji Vinayak Thosar
and
Bawa Kartar Singh.

(From the Department of Physics, Indian Institute of Science, Bangalore, and the Department of Chemistry, Science College, Patna.)

Received July 8, 1937.

1. Introduction.

Pasteur's principle of molecular dissymmetry postulates that enantiomorphous molecular configurations must give identical values for the magnitude of their scalar and vectorial properties, as the *dextro* and *lævo* forms of a compound are related to one another as an object is to its non-superposable *exact* mirror image. In several communications,[1] this identity was established as regards the magnitude of the rotatory power for many such pairs of isomers. In a subsequent communication,[2] the physical identity of the optically active and opposite forms was extended to several scalar properties, such as viscosity, density and refraction. In the present paper, which is a continuation of this series, dealing with work on the physical identity of enantiomers undertaken by one of us, we have extended the application of this principle to the Raman frequencies of the *d* and *l* forms of borneol and camphor. In this study, the racemic forms of these compounds are also included with the object of finding out whether the Raman spectrum of the racemic form is different from that of the *d* and *l* forms and thus throw any light on the mode of union of the *d* and *l* components in a racemate. The study of the viscosity-concentration graphs of the *d*, *l* and *dl* forms of camphor in ethyl alcohol as reported in an earlier paper,[2] showed that they diverge more and more apart with increasing concentration. For concentrations of about 3 per cent. and lower, the values of viscosity for the three forms are identical; but at higher concentrations the racemic form has higher viscosity than the *d* and *l* forms. The existence of the *dl* compound in the case of camphor in solution in ethyl alcohol above 3 per cent. concentration is thus clearly established. The racemic form of camphor in the solid state must be a true compound of the *d* and *l* components in equimolecular proportions. The study of its Raman spectrum in the solid state

as well as that of its opposite and active forms was thought to be of considerable interest. Since borneol is the secondary alcohol corresponding to the ketone, camphor, any differences in their Raman spectra must be ascribed to this change in the chemical structure of the molecule. A similar comparative study of the three forms of borneol is, therefore, also undertaken.

2. *Experimental.*

The technique of the complementary filters, devised by R. Ananthakrishnan,[3] for investigating crystals was employed. The pair of complementary filters used was a concentrated solution of iodine in carbon tetrachloride and an aqueous solution of sodium nitrite of suitable strength. The exciting line was λ 4046 of the mercury arc spectrum. The Raman spectra were photographed on high speed golden isozenith plates and the duration of exposure was 96 hours in every case. A Fuess spectrograph of high light-gathering power was used in this work. The plates were measured by means of a Hilger cross-slide microscope in comparison with an iron-arc spectrum which was recorded in the centre of every picture.

3. *Preparation and Purification of Materials.*

The camphors and borneols were prepared and purified according to methods already given.[4] The melting points and rotatory power of the camphors were as follows :—

	m.p.	$[\alpha]^{35°}_{Hg\ 5461}$	
d-Camphor ..	178°–179°	+ 59·61°	for 33·3 per cent. solution in ethyl alcohol
l-Camphor ..	178°–179°	− 59·41	
dl-Camphor ..	178°	0·0	

The borneols used also gave correct values of the melting point and rotatory power.

The borneols and camphors at first gave a continuous background on the photographic plate, which masked many lines. On recrystallising the compounds three times from ligroin (b.p. 75°–90° C.), the background was sufficiently cleared.

4. *Results.*

Tables I and II record the frequency shifts of the Raman lines, visual estimates of their intensities, I and observed structural characters :— s = sharp, b = broad and d = diffuse.

TABLE I.

Borneols.

Exciting line 4046·5 A.U. $\nu = 24705$ cm.$^{-1}$

Time of exposure 96 hours each.

No.	*Lævo*			*Dextro*			*Racemic*		
	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I
1	24056	649	4*s*	24055	650	4*s*	24055	650	4*s*
2	23968	737	0	23968	737	0	23968	737	0
3	23945	760	0	23945	760	0	23945	760	0
4	23819	886 (?)	0	..	..		..	..	
5	23763	942	0	23763	942	0	23763	942	0
6	23733	972	1	23729	976	1	23727	978	1
7	23628	1077	1	23628	1077	0	23630	1075	0
8	23517	1188	0	23517	1188	0	..	..	..
9	..	..	..	23483	1222	0	23480	1225	0
10	23407	1298	½	23407	1298	½	23407	1298	½
11	23260	1445	2*b*	23265	1440	2*b*	23263	1442	2*b*
12	23227	1478	2*b*	23233	1472	2*b*	23232	1473	2*b*
13	21967	2738	0*b*	21967	2738	0*b*	21967	2738	0*b*
14	21828	2877	2*b*	21833	2872	1	21836	2869	1
15	21783	2922	2	21785	2920	2	21781	2924	2
16	21757	2948*	8*b*	21757	2948*	8*b*	21753	2952*	8*b*
17	21724	2981	1	21724	2981	2	21733	2972	2

Note 1.—* Indicates that the line has also been excited by 4077 A.U.

Note 2.—There is a continuous spectrum superposed on the lines from 14 to 17.

TABLE II.

Camphors.

Exciting line 4046·5 A.U. $\nu = 24705$ cm.$^{-1}$

Time of exposure 96 hours each.

No.	*Lævo*			*Dextro*			*Racemic*		
	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I
1	24056	649*	4*s*	24055	650*	4*s*	24053	652*	4*s*
2	23848	857	2*s*	23855	850	1*s*	23851	854	0
3	23752	953	2*s*	23749	956	1*s*	23757	948	1
4	23462	1243	0	..	..		23462	1243	0
5	23282	1423	0	..	..		..	..	
6	23260	1445	½	..	..		..	..	
7	21837	2868	3*b*	21835	2870	3	21837	2868	3
8	21780	2925*	5	21785	2920*	4	21777	2928*	5
9	21742	2963*	6*b*	21737	2968*	6*b*	21733	2972*	6*b*

Note 1.—* Indicates that the line has also been excited by 4077 A.U.

Note 2.—There is a continuous spectrum superposed on the lines 2868, 2925 and 2963 cm.$^{-1}$

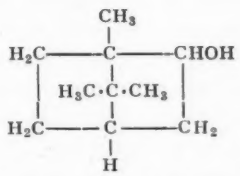
5. *Discussion of Results.*

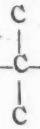
Except for small variations in the spectra of the *dextro* and *lævo* forms of borneol and camphor, which are due to the difference in the quality of the photographs, no appreciable changes have been observed in the position, intensity and structure of the Raman lines in the two enantiomorphous forms of both these compounds. Similar results have been obtained by one of us[5] with the *d* and *l* forms of camphoric acid and its anhydride. Pasteur's principle of molecular dissymmetry, thus, stands firmly established with regard to this new property of matter, resulting from the interaction of molecules with light quanta.

The racemic forms of borneol and camphor give the same Raman lines as the *d* and *l* forms of the respective substances. This result agrees with the fact that the Raman lines due to the vibrations of atoms in the individual molecules of the optically active forms are, in the first approximation, unaffected by the intermolecular forces binding the *d* and *l* molecules forming the racemate. The viscosity measurements[2] at different concentrations of the racemic camphor have definitely indicated that for concentrations above 3 per cent. in ethyl alcohol, the *d* and *l* components form a loosely-bound complex molecule (*dl*) which dissociates into its constituents at lower concentrations. From this it may be concluded that the binding force between *d* and *l* components of the racemate is small and therefore, any intermolecular oscillations arising from this binding could, at best, give only weak Raman lines of low frequency. The sodium nitrite solution in the path of the scattered rays renders frequencies up to about 600* from 4046 A.U., very weak. Due to this and also to the presence of a continuous spectrum in this region, any frequency of this order could well have escaped detection in the present investigation.

The following remarks on the relation between chemical constitution and the characteristic Raman frequencies of the compounds may be made.

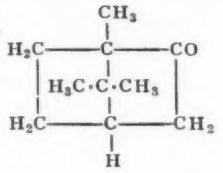
(*a*) *Borneols* :



On an average about seventeen frequencies have been recorded in Table I for the borneols. Out of these, five lines at 2738, 2877, 2922, 2948 and 2981 belong to the valence oscillations and two at 1445 and 1478 to the deformation oscillations of the CH groups. The lines at 886, 942, 972, 1077, 1188 and 1222 may be due either to ring structure or to the C—C vibrations. The line at 649 is the strongest and sharpest line in that region and presumably arises from the symmetrical oscillations of the tetrahedral group  The weak line at 1298 is exactly double this frequency and has, therefore, to be taken as its harmonic.

* The figures given in this paper indicate wave numbers per cm.$^{-1}$

(*b*) *Camphors* :



The structural formula of borneol differs from that of camphor in that the secondary alcohol group CHOH has been replaced by a carbonyl group C = O. In Table II, only nine frequencies have been recorded. The three lines at 2868, 2925 and 2963 must be ascribed to C—H valence vibrations. Two of these (2868 and 2925) are also present in borneol. In spite of the fact that long exposures have been given and the C ↔ H vibrations have been recorded strongly, the δ (CH) frequencies have appeared only feebly in *lævo* camphor. In the *dextro* and racemic forms, their presence could not be detected. This comparative weakness of the δ (CH) frequencies in camphor for equal intensities of the C ↔ H lines in both borneol and camphor is rather surprising.

There are four low frequencies, namely, 649, 857, 953 and 1243 in camphors. Of these, the line at 649 is also found in borneol and is evidently due to the ' neopentyl ' group as indicated for the latter. The other three frequencies differ from those of borneol in that region as may be expected from the difference in their molecular structure. The Raman shifts characteristic of the C = O linkage in camphor could not be detected as it falls in the region of λ 4358 of the mercury arc spectrum. The line due to OH in borneol has also not been recorded. From the complexity of the molecular structure of these two compounds, we should expect many more lines than have been recorded here and a detailed investigation of these substances in the state of solution would be of great interest.

6. *Summary.*

1. The Raman spectra of the *d*, *l* and *dl* forms of borneol and of camphor have been studied in the crystalline state. The spectra of *dextro* and *lævo* forms in both cases are identical, thus supporting Pasteur's Law of Molecular Dissymmetry.

2. The Raman spectra of the *dl* forms of borneol and camphor are also the same as those of their optically active isomers. This supports the view already derived from measurements of viscosity that the *d* and *l* components in a racemic compound are very loosely bound.

3. The most intense shifts in these compounds are those associated with C—H vibrations.

4. An intense and sharp line occurs at about 650 cm.$^{-1}$ in both camphor and borneol and is ascribed to the neopentyl group.

Our thanks are due to Sir C. V. Raman for affording necessary laboratory facilities and for his interest in this work. We also wish to thank Dr. C. S. Venkateswaran and Messrs. R. Ananthakrishnan and B. H. Iyer for valuable assistance.

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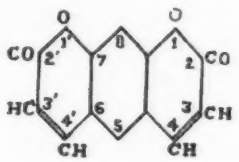
CONSTITUTION OF COUMARINOPYRONES DERIVED FROM 7-HYDROXY-COUMARINS.

By S. Rangaswami
and
T. R. Seshadri.
(From the Department of Chemistry, Andhra University, Waltair.)

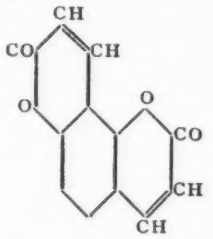
Received July 12, 1937.

During the preparation of 4-methylumbelliferon from resorcinol and ethylacetoacetate using alcoholic hydrogen chloride as the condensing agent[1] it was noticed by us that it was always accompanied by more or less quantities of a complex, sparingly soluble substance. This could be crystallised from hot acetic acid or pyridine and was found to be identical with 4 : 4'-dimethylcoumarinopyrone first prepared in a very small yield by Hantzsch and Zürcher[2] from resorcinol (1 mol.) and ethylacetoacetate (2 mols.) using sulphuric acid as the condensing agent. It has been obtained in better yields more recently by Sen and Chakravarti[3] by condensing 4-methylumbelliferon with ethylacetoacetate in the presence of sulphuric acid. This condensation of 4-methylumbelliferon does not succeed with alcoholic hydrogen chloride which however produces a good yield of the coumarinopyrone by the direct reaction of resorcinol and ethylacetoacetate.

Besides obtaining the above dimethylcoumarinopyrone, Sen and Chakravarti have condensed a few other umbelliferon derivatives with malic acid and ethylacetoacetate and obtained the corresponding coumarinopyrones. The exact constitutions of these compounds were left undecided by them. There are two alternatives for the formation of the new pyrone ring. The compound may be the linear coumarino-7 : 6-α-pyrone (I) or the angular coumarino-7 : 8-α-pyrone (II). Since this question is closely connected with work in progress in these laboratories, an attempt has now been made to settle it in as unambiguous a manner as possible.



I



II

The above compounds have received different names at different times. Hantzsch and Zürcher's name ' dicoumarins ' is obviously unsuitable. Sen and Chakravarti called them ' coumaropyrones '. Under this name they are likely to be mistaken for coumarone compounds, a large number of which occur frequently in nature. Hence they are now named ' coumarino-α-pyrones '. The positions in the coumarin ring are numbered as usual from 1 to 8 and those in the second pyrone ring are marked with a dash. As will be easily evident from a scrutiny of the two isomers there is only one possible way of naming the linear compound which is symmetrical, whereas there are two possible names for the angular variety as (1) coumarino-7 : 8-α-pyrone or (2) coumarino-5 : 6-α-pyrone.

Umbelliferon was converted into 7-hydroxycoumarin-8-aldehyde by Späth and others[4] using hexamethylenetetramine and its constitution was established by them by synthesising angelicin from it. This aldehyde has now been subjected to the Perkin's condensation using sodium acetate and acetic anhydride giving rise to coumarino-7 : 8-α-pyrone (II). The aldehyde of 4-methylumbelliferon has been made by adopting the same method. By analogy this could be assumed to be the 8-aldehyde. But we have made the constitution surer by reducing it with hydrogen in the presence of palladium-charcoal to the corresponding methyl derivative. This had been found to be identical with 4 : 8-dimethyl-7-hydroxycoumarin which could be synthesised from 2-methylresorcinol by condensation with ethylacetoacetate by the Pechmann's method. The aldehyde, therefore, becomes 4-methyl-7-hydroxycoumarin-8-aldehyde and gives rise to 4-methyl-coumarino-7 : 8-α-pyrone by treatment with sodium acetate and acetic anhydride.

By the condensation of malic acid with umbelliferon in the presence of sulphuric acid a product (A) is obtained melting at about 246° C. (not sharp) as recorded by Sen and Chakravarti. It resembles coumarino-7 : 8-α-pyrone very closely in properties. But the latter melts about 12° higher (258–60° C.) and the mixed melting point was in between. On closely examining (A), however, it was realised that it was a mixture of two substances which could be separated by virtue of the marked difference in solubility between them. The more easily soluble fraction was the major portion (95 per cent.) and was found to be identical with coumarino-7 : 8-α-pyrone in all respects. The less easily soluble fraction melted at a much higher temperature (334–35° C.). It is isomeric with the major product and is obviously the linear coumarino-7 : 6-α-pyrone. This is in agreement with the general observation that linear isomers are more sparingly soluble and melt at a higher temperature than the corresponding angular ones. [Compare psoralen and isopsoralen

(angelicin).[5]] The conclusion could therefore be drawn that when two alternatives are available the predominant tendency is to form the angular compound. However, the formation of the linear variety is also possible, though to a small extent.

The product obtained from 4-methylumbelliferon and malic acid was found to resemble 4-methylcoumarino-7 : 8-α-pyrone in all properties ; the melting points were identical and the mixed melting point undepressed. It seemed to be a single compound and no isomer could be isolated as in the previous case, in spite of repeated attempts at fractionation.

The condensations of umbelliferon and 4-methylumbelliferon with ethylacetoacetate have also been examined. Umbelliferon did not undergo any condensation with either sulphuric acid or alcoholic hydrogen chloride. In the presence of sulphuric acid 4-methylumbelliferon and ethylacetoacetate give only a poor yield of the product which can be obtained in better quantities by the action of alcoholic hydrogen chloride on resorcinol and ethylacetoacetate. The substance has a sharp melting point which does not change by repeated recrystallisations, and it could not be separated into two compounds by fractional crystallisation. It is, therefore, described as 4 : 4′-dimethylcoumarino-7 : 8-α-pyrone.

Experimental.

7-Hydroxycoumarin-8-aldehyde[4] was prepared according to the directions given by Späth. The smallness of the yield was found to be due to the production of a large amount of a complex, sparingly soluble, yellow by-product. When large quantities of umbelliferon were employed (Späth, 20 gm.) the by-product used to be obtained in disproportionately high yield, and the yield of the aldehyde was unsteady and poor. With smaller quantities, about 5 gm., the yield was consistently about 0·6 gm.

Coumarino-7 : 8-α-pyrone.—The above aldehyde (0·5 g.) was heated with fused sodium acetate (1 g.) and acetic anhydride (10 c.c.) for 7 hours in an oil-bath kept at 180° C. The product was poured into cold water (300 c.c.) and the solid that separated on leaving overnight was filtered and recrystallised first from glacial acetic acid and then from pyridin. It came out as rhombic plates and needles melting at 258–60°C., to a brown liquid. The yield was 0·5 g. [Found : C, 67·1 % ; H, 3·1 % ; $C_{12}H_6O_4$ requires C, 67·3 % ; H, 2·8 %.]

The substance is sparingly soluble in ether, alcohol and benzene and dissolves fairly easily in acetic acid and pyridin. It is unaffected by aqueous sodium carbonate and dissolves only very slowly in aqueous ammonia and sodium hydroxide in the cold and more rapidly on heating.

Condensation of malic acid with umbelliferon.—This condensation was effected according to the method of Sen and Chakravarti[3] and a fairly good yield of a colourless crystalline product (55%) was obtained. It was noticed that if hot ammonia should be employed for removing unchanged umbelliferon, considerable loss of the coumarinopyrone was sustained and that maceration with cold dilute ammonia was sufficient. The product was once crystallised from glacial acetic acid. It was quite crystalline and almost colourless. But the melting point was not sharp, the mass sintering from 242° C. and melting down completely at about 248° C. (Sen and Chakravarti, 245–50° C.). Ordinary methods of crystallisation did not raise the melting point appreciably.

Separation of the mixture.—By boiling the product with an insufficient quantity of acetic acid or pyridin and filtering hot a small amount of a sparingly soluble fraction was left behind on the filter. This was kept separately. The solution now deposited a colourless crystalline solid which melted at about 255° C. On further crystallisation from pyridin it gave rhombic plates and needles melting at 258–60° C., and was found to be identical with coumarino-7 : 8-α-pyrone obtained from 7-hydroxycoumarin-8-aldehyde. A mixed melting point showed no depression. [Found : C, 67·3 % ; H, 3·0 % ; $C_{12}H_6O_4$ requires C, 67·3 % ; H, 2·8 %.]

Isolation of coumarino-7 : 6-α-pyrone.—The sparingly soluble fraction on the filter melted above 300° C. It was markedly less soluble than the other product in all organic solvents. It could however be crystallised from boiling pyridin as colourless rectangular tablets and prisms. The substance has a tendency to come out invariably in hard big crystals. It melts at 334–35° C. with sintering at about 330° C. and then decomposes. In its reaction towards alkali it resembles coumarino-7 : 8-α-pyrone. [Found : C, 67·2 % ; H, 3·0 % ; $C_{12}H_6O_4$ requires C, 67·3 % ; H, 2·8 %.] The yield of this compound was about 5% of the crude mixture obtained from the condensation, the rest being the 7 : 8 isomer.

4-Methyl-7-hydroxycoumarin-8-aldehyde.—This was prepared from 4-methylumbelliferon by the same method as was employed with umbelliferon. The substance was obtained as colourless thick plates on evaporating the final ether extract. When recrystallised from aqueous alcohol it melted at 176° and the yield was found to be 0·6 g. from 4·5 g. of the starting material. [Found : C, 64·3% ; H, 4·0 % ; $C_{11}H_8O_4$ requires C, 64·7 % ; H, 3·9 %.] The substance was easily soluble in the ordinary solvents like ether and alcohol. An aqueous solution gave an intense violet colour with ferric chloride. It formed a phenyl-hydrazone which crystallised out from alcohol

as long fine needles melting at 251–52° C., and a semicarbazone crystallising as needles and narrow plates which does not melt below 300° C. but changes colour on heating—colourless at the ordinary temperature, turning yellow at about 180° C. and greenish blue at about 300° C.

Reduction to 4 : 8-*dimethyl*-7-*hydroxycoumarin.*—The above aldehyde was dissolved in glacial acetic acid, treated with palladium charcoal (prepared from animal charcoal and palladium chloride) and shaken in an atmosphere of hydrogen till 2 molecular proportions of the gas were absorbed.[6] The solution was then filtered and the solvent removed by distillation under reduced pressure. The residue was then treated with water, the remaining acid just neutralised with sodium carbonate and the reduction product removed by extraction with ether. The ether solution was then shaken with a saturated solution of sodium bisulphite to remove any unreduced aldehyde and washed with water. Evaporation of the solvent gave 4 : 8-dimethylumbelliferon which on recrystallisation from alcohol appeared as rectangular plates and tablets, melting at 257–58° C. [Found : C, 69·5 % ; H, 5·4 % ; $C_{11}H_{10}O_3$ requires C, 69·5 % ; H, 5·3 %.] A mixture of this with the specimen made from 2-methylresorcinol (see below) melted at the same temperature.

Preparation of 4 : 8-*dimethyl*-7-*hydroxycoumarin from* 2-*methylresorcinol.*—2-methylresorcinol was prepared from β-resorcylic acid by following the method adopted by Robinson and Shah[7] for 2-ethylresorcinol. The acid was smoothly converted into the methyl ester by boiling with anhydrous methyl alcohol containing 5–6% hydrogen chloride or concentrated sulphuric acid for about 4 hours. It was then methylated using methyl iodide (5 mols.) and methyl alcoholic potash (4 mols.). The resulting product was macerated with cold dilute sodium hydroxide. The portion insoluble in alkali was found to be methyl 3-methyl-4-methoxy-β-resorcylate. It crystallised from methyl alcohol as rectangular tablets, melting at 76–77° C. By direct treatment with concentrated hydriodic acid this ester gave 2-methylresorcinol by simultaneous hydrolysis, decarboxylation and demethylation. But the yield and purity were not satisfactory. Therefore, the ester was hydrolysed with alcoholic potash just as the previous workers have done and the resulting acid subjected to the action of hydriodic acid.[7,8] 2-Methylresorcinol was easily obtained pure on recrystallisation from benzene—light petroleum mixture from which it was deposited as elongated prisms, melting at 115–16° C. It gave the fluorescein reaction with phthalic anhydride.

A mixture of equimolecular proportions of 2-methylresorcinol and ethyl-acetoacetate was treated with twice the weight of concentrated sulphuric

acid and allowed to stand overnight at the laboratory temperature. 4 : 8-dimethyl-7-hydroxycoumarin was isolated by pouring the mixture into water, filtering and washing with water. It crystallised from alcohol as thin rectangular plates, melting at 257–58° C. [Found : C, 69·5 % ; H, 5·2 % ; $C_{11}H_{10}O_3$ requires C, 69·5% ; H, 5·3%] and was found to be identical with the sample obtained above by the reduction of 4-methyl-7-hydroxycoumarin-8-aldehyde.

4-*Methylcoumarino*-7 : 8-*α-pyrone*.—4-Methyl-7-hydroxycoumarin-8-aldehyde was treated with sodium acetate and acetic anhydride for 7 hours at 180° C. and the product isolated as usual. It crystallised from glacial acetic acid as colourless fine needles, melting at 304–5° C. to a brown liquid. [Found: C, 67·8 % ; H, 3·9 % ; $C_{13}H_8O_4$ requires C, 68·4 % ; H, 3·5 %.]

Condensation of malic acid with 4-methyl-7-hydroxycoumarin.—The mixture of the two was treated with concentrated sulphuric acid and heated at 100° C. for 4 hours (Sen and Chakravarti[3]). The solid obtained on pouring it into water was digested with cold dilute ammonia to remove any unchanged hydroxycoumarin and recrystallised from glacial acetic acid. In every respect it was identical with 4-methylcoumarino-7 : 8-α-pyrone. The melting point of the mixture was undepressed. A close examination of the crude product by the method of fractional crystallisation did not reveal any heterogeneity.

4 : 4′-*Dimethylcoumarino*-7 : 8-*α-pyrone*.—The following methods were examined. Since only one substance could be obtained as the product it could be taken to be 4 : 4′-dimethylcoumarino-7 : 8-α-pyrone—m.p. 333–5° C. All properties agree with the description given by Sen and Chakravarti.

Resorcinol (1 mol.) condensed with ethylacetoacetate (2 mols.) to produce an insignificant yield of the coumarinopyrone when cold sulphuric acid was used and 20 per cent. yield when alcoholic hydrogen chloride was used as the condensing agent. With the latter condensing agent the yield was 5–6 per cent. when only one molecule of ethylacetoacetate was employed. With 4-methylumbelliferone (1 mol.) and ethylacetoacetate (1 mol.) the yield of the coumarinopyrone was negligible in the presence of alcoholic hydrogen chloride and 10–15 per cent. with sulphuric acid.

Summary.

When umbelliferon condenses with malic acid two isomeric compounds are formed. The angular coumarino-7 : 8-α-pyrone is the major product (95%) and its constitution is established from its preparation from umbelliferon-8-aldehyde by the Perkin's reaction. The second compound which should be the linear coumarino-7 : 6-α-pyrone is formed in a very small yield only (5%). Under the same conditions 4-methylumbelliferon produces

only one compound whose constitution as 4-methylcoumarino-7 : 8-α-pyrone is arrived at from its independent synthesis from 4-methylumbelliferon-8-aldehyde. The constitution of this aldehyde is deduced not only from analogy but also from its reduction to 4 : 8-dimethyl-7-hydroxycoumarin which has been prepared from 2-methylresorcinol and ethylacetoacetate. 4-Methylumbelliferon and ethylacetoacetate also give only one compound which is given the constitution 4 : 4′-dimethylcoumarino-7 : 8-α-pyrone. This compound has been found to be produced in good yield from resorcinol and ethylacetoacetate in the presence of alcoholic hydrogen chloride.

It is concluded that the angular isomer is the one invariably and most predominantly formed though the formation of the linear variety is not altogether precluded.

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ON SERIES OF JACOBI-POLYNOMIALS AND DEFINITE INTEGRALS INVOLVING BESSEL FUNCTIONS.

By N. G. Shabde, D.Sc.
(College of Science, Nagpur.)

Received May 10, 1937.
(Communicated by Mr. N. S. Nagendra Nath.)

1. *Introduction.*—G. N. Watson[1] has expressed the sum of an infinite series involving two Jacobi-polynomials, of the type

$$\sum_{n=0}^{\infty} a_n \, P_n^{(\alpha,\beta)} (\cos 2\phi) \, P_n^{(\alpha,\beta)} (\cos 2\Phi)$$

where a_n is a constant, as an integral of elementary functions. A. Erdélyi[2] has recently obtained the sum of the same series in terms of Appell's function F_3. W. N. Bailey[3] also has summed a similar series. The object of this note is to find the sums of some more series of the above type and to evaluate some definite integrals involving Bessel functions.

2. Let

$$c_n = (2n + \alpha + \beta + 1) \frac{n! \, \Gamma(n+\alpha+\beta+1)}{2^{\alpha+\beta+1} \, \Gamma(n+\alpha+1) \, \Gamma(n+\beta+1)}.$$

Then we have[4]

$$\left.\begin{aligned} &2^{\alpha+\beta+2} \sin^{\alpha}\phi \sin^{\alpha}\Phi \cdot \cos^{\beta}\phi \cos^{\beta}\Phi \times \\ &\quad \times \sum_{n=0}^{\infty} (-1)^n c_n \, J^{(z)}_{2n+\alpha+\beta+1} \, P_n^{(\alpha,\beta)} (\cos 2\phi) \cdot P_n^{(\alpha,\beta)} (\cos 2\Phi) \\ &= z \, J_{\alpha}(z \sin\phi \sin\Phi) \, J_{\beta}(z \cos\phi \cdot \cos\Phi) \end{aligned}\right\} \qquad (2.\ 1)$$

Multiply both the sides of (2. 1) by $e^{-cz} \cdot z^{\alpha+\beta}$ and integrate with respect to z between 0 and ∞. We get

$$\left.\begin{aligned} &2^{\alpha+\beta+2} \sin^{\alpha}\phi \sin^{\alpha}\Phi \cdot \cos^{\beta}\phi \cos^{\beta}\Phi \cdot \sum_{n=0}^{\infty} (-1)^n c_n \, P_n^{(\alpha,\beta)} (\cos 2\phi) \, P_n^{(\alpha,\beta)} (\cos 2\Phi) \times \\ &\quad \times \int_0^{\infty} J^{(z)}_{2n+\alpha+\beta+1} \, e^{-cz} \cdot z^{\alpha+\beta} \, dz \\ &= \int_0^{\infty} z^{\alpha+\beta+1} \, e^{-cz} \, J_{\alpha}(z \sin\phi \sin\Phi) \, J_{\beta}(z \cos\phi \cos\Phi) \, dz \end{aligned}\right\} \qquad (2.\ 2)$$

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[1] "Notes on Generating Functions of Polynomials: (4) Jacobi," *Journ. Lond. Math. Soc.*, 1934, 9, 22–28.

[2] "Über die erzeugende Funktion der Jacobischen Polynome," *Journ. Lond. Math. Soc.*, 1937, 12, 56–57.

[3] "Generalized Hypergeometric Series," *Cambridge Tracts in Mathematics and Mathematical Physics*, No. 32, p. 102, Ex. 19.

[4] G. N. Watson, *loc. cit.*

To evaluate the integral on the left of (2. 2) we make use of a known result[5] and to evaluate the integral on the right we use a general integral evaluated by A. Erdélyi.[6] This gives us

$$\left.\begin{aligned}\sum_{n=0}^{\infty}(-1)^n\cdot c_n\frac{\Gamma 2(n+\alpha+\beta+1)\cdot 2F_1[n+\alpha+\beta+1,\ n,\ 2n+\alpha+\beta+2,\ \frac{1}{1+c^2}]}{\Gamma(2n+\alpha+\beta+2)\ (1+c^2)^{n+\alpha+\beta+1}}\\ \times\ P_n^{(\alpha,\beta)}(\cos 2\phi)\ P_n^{(\alpha,\beta)}(\cos 2\Phi)\\ =\frac{\Gamma 2(\alpha+\beta+1)\cdot(c+i\cos\overline{\phi-\Phi})^{-2(\alpha+\beta+1)}}{\Gamma(\alpha+1)\ \Gamma(\beta+1)\cdot 2^{2(\alpha+\beta+1)}}\times\\ \times\ F_2\left[2(\alpha+\beta+1)\,;\,\alpha+\tfrac{1}{2},\beta+\tfrac{1}{2}\,;\,2\alpha+1,\,2\beta+1\,;\,\frac{2i\sin\phi\sin\Phi}{c+i\cos(\phi-\Phi)},\right.\\ \left.\frac{2i\cos\phi\cos\Phi}{c+i\cos(\phi-\Phi)}\right].\end{aligned}\right\} \tag{2. 3}$$

This result is true for R $(c\pm i)>0$ and R $(2\alpha+2\beta+2)>0$. Proceeding in the same way, multiplying both sides of (2. 1) by $e^{-cz}z^{\alpha+\beta-1}$ and integrating with respect to z between 0 and ∞ we have by means of known results

$$\left.\begin{aligned}\sum_{n=0}^{\infty}(-1)^n\cdot c_n\frac{\Gamma(2n+2\alpha+2\beta+1)2F_1[n+\alpha+\beta+\frac{1}{2},n+1,2n+\alpha+\beta+2,\frac{1}{1+c^2}]}{\Gamma(2n+\alpha+\beta+2)\ (1+c^2)^{n+\alpha+\beta+\frac{1}{2}}}\times\\ \times\ P_n^{(\alpha,\beta)}(\cos 2\phi)\,P_n^{(\alpha,\beta)}(\cos 2\Phi)\\ =\frac{\Gamma 2(\alpha+\beta)}{2^{2(\alpha+\beta+1)}\,\Gamma(\alpha+1)\,\Gamma(\beta+1)}\,(c+i\cos\overline{\phi-\Phi})^{-2(\alpha+\beta)}\times\\ \times\ F_2\left[2(\alpha+\beta)\,;\,\alpha+\tfrac{1}{2},\beta+\tfrac{1}{2}\,;\,2\alpha+1,\,2\beta+1\,;\,\frac{2i\sin\phi\sin\Phi}{c+i\cos(\phi-\Phi)},\right.\\ \left.\frac{2i\cos\phi\cos\Phi}{c+i\cos\overline{\phi-\Phi}}\right]\end{aligned}\right\} \tag{2. 4}$$

(2. 4) is true for R $(c\pm i)>0$ and R $(2\alpha+2\beta)>0$.

Another summation can be effected by using (2. 1) with the known results

$$\left.\begin{aligned}&\text{(i)}\quad\int_0^{\infty}J_n(ax)\,x^q\,dx=\frac{2^q}{a^{q+1}}\frac{\Pi\left(\frac{n+q-1}{2}\right)}{\Pi\left(\frac{n-q-1}{2}\right)},\qquad q<\tfrac{1}{2}\\ &\text{(ii)}\quad\int_0^{\infty}J_m(bx)\,J_n(ax)\,x^{m-n+1}\,dx=\frac{b^m}{a^n}\,\frac{(a^2-b^2)^{n-m-1}}{2^{n-m-1}\,\Pi(n-m-1)}\ \text{if } a>0\\ &\qquad\text{and }=0\text{ if } a<b\,;\ n>m>-1.\end{aligned}\right\}$$

[5] Watson, *Theory of Bessel Functions*, p. 385.

[6] A. Erdélyi, "Über einige bestimmte Integrale, in denen die Whittakerschen $M_{k,m}$-Funktionen auftreten," *Math. Zeitschrift*, 1936, **40**, 693–702.

Taking $\beta > \alpha > -\frac{1}{2}$, the final result is

$$\left.\begin{aligned}&\sum_{n=0}^{\infty}(-1)^n . c_n \frac{\Gamma(n+\alpha+1)}{\Gamma(n+\beta+1)} P_n^{(\alpha,\beta)}(\cos 2\phi)\, P_n^{(\alpha,\beta)}(\cos 2\Phi)\\ &= \frac{(\cos^2\phi\cos^2\Phi - \sin^2\phi\sin^2\Phi)^{\beta-\alpha-1}}{2^{\alpha+\beta+1}\Gamma(\beta-\alpha)(\cos\phi\cos\Phi)^{2\beta}}\\ &\qquad\qquad \text{if } \cos\phi\cdot\cos\Phi > \sin\phi\sin\Phi\end{aligned}\right\} \quad (2.5)$$

and $= 0$ if $\cos\phi.\ \cos\Phi < \sin\phi\sin\Phi$

3. Bailey[7] gives the expansion

$$J_\nu(z\cos\theta)\, J_\nu(z\sin\theta) = \sum_{r=0}^{\infty} \frac{(\frac{1}{4}z\sin 2\theta)^{\nu+2r}}{r!\,\Gamma(\nu+r+1)} J_{\nu+2r}(z) \quad (3.1)$$

From this, multiplying both sides by $\sin^p\theta\cos^q\theta$, p and q being both positive and integrating with respect to θ between 0 and $\frac{\pi}{2}$, we get the integral

$$\left.\begin{aligned}&\int_0^{\frac{\pi}{2}} J_\nu(z\cos\theta)\, J_\nu(z\sin\theta)\sin^p\theta\cdot\cos^q\theta\cdot d\theta\\ &= \sum_{r=0}^{\infty}\left(\frac{z}{4}\right)^{\nu+2r}\cdot\frac{2^{\nu+2r}}{r!\,\Gamma(\nu+r+1)}\cdot\frac{1}{2}\cdot\frac{\Gamma\left(\frac{\nu+p+2r+1}{2}\right)\Gamma\left(\frac{\nu+q+2r+1}{2}\right)}{\Gamma\left(\frac{2\nu+p+q+4r+2}{2}\right)} J_{\nu+2r}(z)\end{aligned}\right\} \quad (3.2)$$

This result is true for R $(\nu) > -1$.

Again using Hardy's[8] result

$$\int_0^{\infty} J_n(z)\cdot z^{-1}\exp(-2kz^{-1})\, dz = 2J_n(2\sqrt{k})\, K_n(2\sqrt{k}) \quad (3.3)$$

with the Bailey's expansion[9]

$$\left.\begin{aligned}&(\tfrac{1}{2}z)^{\kappa-\mu-\nu} J_\mu(az)\, J_\nu(bz)\\ &= \frac{a^\mu\cdot b^\nu}{\Gamma(\mu+1)\,\Gamma(\nu+1)}\sum_{n=0}^{\infty}\frac{(\kappa+2n)\,\Gamma(\kappa+n)}{n!} F_4[-n, \kappa+n; \mu+1, \nu+1; a^2, b^2]\\ &\qquad\qquad \times J_{\kappa+2n}(z)\end{aligned}\right\} \quad (3.4)$$

we have

$$\left.\begin{aligned}&\int_0^{\infty} z^{\kappa-\mu-\nu-1} J_\mu(az)\, J_\nu(bz)\, e^{-\frac{2k}{z}}\, dz\\ &= \frac{2^{\kappa-\mu-\nu}\, a^\mu\cdot b^\nu}{\Gamma(\mu+1)\,\Gamma(\nu+1)}\sum_{n=0}^{\infty}\frac{(\kappa+2n)\,\Gamma(\kappa+n)}{n!} F_4[-n, \kappa+n; \mu+1,\\ &\qquad\qquad \nu+1; a^2, b^2]\times J_{\kappa+2n}(2\sqrt{k})\, K_{\kappa+2n}(2\sqrt{k})\end{aligned}\right\} \quad (3.5)$$

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[7] "On the product of two legendre polynomials with different arguments," *Proc. London Math. Soc.*, series 2, **41**, Part 3, 215–20; *see* p. 219, formula (5. 2).

[8] *Messenger of Maths.*, **56**, 190.

[9] "Some expansion in Bessel Functions involving Appell's Function F_4," *Quarterly Journal of Maths.* (Oxford Series), **6**, 233–38.

THE FLAME SPECTRA OF SOME ALIPHATIC HALIDES—PART I.

(1) Methyl Iodide.

By W. M. Vaidya, B.Sc. (Lond.), Ph.D. (Lond.),

Fergusson College, Poona.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received August 6, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In the course of a detailed examination of the spectra of the flames of carbon compounds, the spectra of the flames of some substituted halogen compounds of methane and ethylene were included for comparative purposes. It was then felt that a more systematic investigation of their spectra might lead to interesting results. The present paper and the following ones give an account of the results obtained in such an investigation.

It has been found that the flame of methyl iodide shows in addition to the well-known bands of CH, C_2 and HO, a number of bands in the visible which do not seem to have been recorded before. For convenience of reference they may be termed " The methyl iodide flame bands ". They are degraded towards the red and some 35 bands have been measured in the visible. They have been found to belong to two systems, A and B, with one level common. With the evidence at present available they have been attributed to I–O.

2. Experimental Details.

Methyl iodide does not burn by itself even when the combustion is supported by oxygen. It was, therefore, mixed with methyl alcohol whose spectrum had already been studied before, and this mixture was placed in a pyrex tube, one end of which was closed and the other drawn to a narrow neck. When a wick dipping in the liquid was lighted copious iodine fumes were given out. This simple arrangement was unsuitable for long exposures which were required to get fair intensity of the bands on a photographic plate.

Identical bands were obtained when common gas mixed with methyl iodide vapour was burnt. Attention was therefore directed towards brightening this flame. A two-way blow-pipe was found convenient. A gentle

current of common gas was bubbled through methyl iodide placed in a small wash-bottle. The mixture flowed through the outer nozzle of the blow-pipe while through the inner one was blowed a current of oxygen from a gas cylinder. With no oxygen coming through the inner nozzle, the flame was somewhat luminous, the upper portion showing violet iodine colour accompanied by fumes of iodine. The flame bands were confined to the central portions of the flame and rather faint. The flame became more and more non-luminous as the quantity of oxygen was increased. By experience it was found that the flame bands were bright and the flame was quite steady as well when the quantity of oxygen coming through the inner nozzle was such that the flame developed the following four regions :—

(1) Just above the inner nozzle, a small bluish-green inner cone as the inner cone of the Bunsen flame and above it a luminous spot above $\frac{1}{2}$ cm. in diameter. If the quantity of oxygen was increased, this luminous spot was replaced by the extended inner cone which tended to make the flame unsteady.

(2) Above this luminous spot, an ill-defined greenish region 5 cm. in length and $\frac{1}{2}$ cm. in breadth. The flame bands were bright at the central portions of this green region and less bright at the upper and lower portions. In the lower regions, the flame bands were accompanied by the C_2 and the CH bands. The middle portion was therefore focussed on the slit of the spectrograph.

(3) The upper most parts of the flame consisting of iodine vapours.

(4) A pale blue mantle surrounding the whole flame as in the Bunsen flame.

When the quantity of oxygen was considerably increased, the flame made a roaring noise and appeared extremely greenish in colour. The flame had only two cones, a small bright inner cone which gave a spectrum identical with that of the inner cone of the Bunsen flame and an extended outer cone which gave the new flame bands. This type of flame was very unsteady and so unsuitable for long exposures.

To lessen the amount of methyl iodide consumed in the combustion a mixture of methyl iodide and methyl alcohol was always used instead of pure methyl iodide. To diminish it still further, the mixture was surrounded by ice ; if too great a quantity of methyl iodide came in the flame, the flame tended to be extinguished.

In the first instance, photographs of the spectrum of the flame of methyl iodide were taken with a small quartz spectrograph (Hilger's E 31). When the preliminary experiments revealed the existence of bands of

unknown origin in the visible, a glass spectrograph made by Feuss and which is extensively used in Sir C. V. Raman's Laboratory for the study of the Raman effect was utilised for further experiments. For the purposes of measurement, Hilger's E1 spectrograph was used with the iron arc as the source of reference lines.

With air blown through, exposures of nearly 50 hours were necessary to take photographs of the spectrum on the Feuss spectrograph; with oxygen however, this period was reduced to 5 hours. For E1, 15 hours were sufficient to photograph most of the fairly intense bands on Ilford's Special Rapid Panchromatic plates when oxygen supported the combustion. A concave mirror placed behind the flame so as to reflect light from behind the flame on to the slit of the spectrograph materially helped to reduce the time of exposure.

Some attempts have been made to obtain the bands in experiments on discharges through various iodine compounds in vacuum tubes but so far without success.

3. *Description of the Spectrum.*

The spectrum of the flame of methyl iodide mixed with oxygen includes the well-known water vapour bands at λ 3064, λ 2811, λ 2608, etc., and the other bands called the methyl iodide flame bands. When that portion of the flame where the new bands were most intense was not exactly focussed on the slit, the CH and the C_2 bands also appeared. Great care was therefore taken to focus the proper region so as to have only the methyl iodide flame bands without the CH and the C_2 bands.

The methyl iodide flame bands extend from about λ 5900 to about λ 4260 and are degraded towards the red. In this region some 35 bands have been measured. There are indications of several faint bands beyond λ 5900 but they were too faint for satisfactory measurements. Even in the region λ 4260–λ 5900 a few bands have been omitted as being unsuitable for accurate measurements owing to their faintness and rather diffuse appearance. The general appearance of the bands may be gathered from Plate I. The bands of the B system are similar in appearance to those in the A system and there is no overlapping between them. With the dispersion employed there were no distinct signs of resolution of the structure of the individual bands.

4. *Wave-lengths of the Methyl iodide flame Bands.*

The results of the measurements are collected in Table I. The figures in the brackets are the intensities of the bands.

TABLE I.

Band-system A.		Band-system B.	
λ	ν	λ	ν
4267·8 (4)	23426	4838·5 (8)	20664
4296·2 (3)	23271	4960·4 (4)	20155
4322·4 (1)	23130 (Doubtful)	4997·4 (3)	20006
4353·7 (5)	22964	5031·2 (2)	19871
4384·3 (4)	22803	5071·2 (2)	19715
4426·6 (2)	22585	5085·8 (2)	19658
4445·9 (5)	22487	5125·9 (6)	19504
4485·0 (7)	22291	5198·3 (3)	19230
4549·2 (5)	21977	5301·8 (6)	18857
4564·8 (3)	21902	5339·7 (3)	18723
4583·0 (10)	21815	5376·5 (2)	18595
4621·1 (6)	21635	5488·9 (5)	18215
4660·3 (3)	21454	5522·6 (4)	18103
4686·2 (8)	21334	5556·0 (2)	17995
4725·6 (6)	21156	5686·0 (4)	17582
4757·8 (4)	21013	5717·4 (2)	17487
4780·5 (4)	20913		
4822·8 (3)	20731		

5. *Analysis of the Bands.*

The bands of both the systems can be arranged in the usual way in a v', v'' scheme as is shown in Tables II (*a*) and II (*b*). In both the systems there is no overlapping and therefore no difficulty was experienced in

locating the "boundary progressions"; the band in the left-hand corner was hence chosen as the 0,0-band.

The bands of the system A can be represented approximately by the formula

$$\nu \text{ head} = 22487 + (321{\cdot}6\,v' - 7{\cdot}3\,v'^2) - (525{\cdot}5\,v'' - 10{\cdot}5\,v''^2)$$

and those of the system B by the formula

$$\nu \text{ head} = 20155 + (517{\cdot}9\,v' - 6{\cdot}3\,v'^2) - (665{\cdot}7\,v'' - 5{\cdot}9\,v''^2).$$

Considering the difficulties in accurate measurements of the exact positions of the heads of the bands owing to their diffuse nature, the identity of the G″ (v'') function of the system A with that of G′ (v') function of the system B is sufficiently close. The identity is still better revealed if Δ G″ ($\frac{1}{2}$) (511 cm.$^{-1}$), Δ G″ ($2\frac{1}{2}$) (481 cm.$^{-1}$) of the system A are directly compared with Δ G′ ($\frac{1}{2}$) (510 cm.$^{-1}$), Δ G′ ($2\frac{1}{2}$) (485 cm.$^{-1}$) of the system B. This shows that the initial level of the system A is the same as the final level of the system B.

The Condon intensity parabolas for both the systems are such as are appropriate to them.

Attention may be drawn to a band existing at λ 4647·3 (6), ν 21513, which does not seem to belong to the methyl iodide flame bands for it possesses fine rotational structure while the latter do not with the dispersion employed. It is degraded towards the red. Its exact origin, however, is unknown.

SYSTEM A. TABLE II (*a*).

v' ↓ \ v'' →	0	1	2	3	4	5	6
0	22487(5)	21977(5)	×				
	510						
	316	*314*					*315*
1	22803(4)*512*	22291(7) *476*	21815(10)	21334(8)			
			481				*298*
		294		*301*			
2	×	22585(2)		21635(6)	21156(6)	20731(3)	
				479	*425*		
				267	*298*	*282*	*282*
3	23426(4)	×		21902(3)	21454(3)	21013(4)	
				448	*441*		
4		23271(3)					20913(4)
	511	*476*	*481*	*464*	*433*		

Unclassified.

λ 4353·7(5) ν 22964.

+ Bands, doubtful being too faint.

SYSTEM B. TABLE II (*b*).

v' ↓ \ v'' →	0	1	2	3	4	5	
0	20155(4)	19504(6)	18857(6) *642*	18215(5) *633*	17582(4)		
	651	*647*					
	509	*502*		*508*	*521*		*510*
1	20664(8) *658*	20006(3)		18723(3) *620*	18103(4) *616*	17487(2)	
				507	*492*	*508*	*502*
2			19871(2) *641*	19230(3) *635*	18595(2) *600*	17995(2)	
				485			*485*
3				19715(2)			
	655	*647*	*642*	*629*	*608*		

Unclassified λ 5085·8(2) ν 19658.

6. The Emitter of the Bands.

It is certain that iodine is one of the atoms constituting the emitter of the methyl iodide flame bands because not only the bands in question appear when methyl iodide burns but also even when a small quantity of pure iodine is held in the outer cone of the Bunsen flame, in which case they can be identified when seen through a direct vision spectroscope. The emitter can therefore be either (1) I_2, (2) C–I, or (3) I–O.

I_2 has 5 band-systems[1] corresponding to the transitions :

(1) A $^1{}_u \leftarrow X\ ^1\Sigma^+ g$
(2) B $^{0+}{}_u \rightleftharpoons X\ ^1\Sigma^+ g$
(3) C $\rightleftharpoons X\ ^1\Sigma^+ g$
(4) C′ $\rightleftharpoons X\ ^1\Sigma^+ g$
(5) D $\leftarrow X\ ^1\Sigma^+ g$

but the constants of any of them do not seem to bear any relationship to those in the formulæ representing the bands under discussion. The possibility of I_2 as being the emitter can, therefore, be ruled out.

The ground frequency of C–I vibration in CH_3I as determined from other spectroscopic data is 532 cm.$^{-1}$ [2] Since the frequency in the excited state of the B band-system is 524 cm.$^{-1}$, CI cannot be the emitter of the methyl iodide bands. Moreover, if the bands were due to CI they would be expected to show some similarity in appearance to C–Cl bands which have been observed by Jevons[3] in a discharge through vacuum tubes in CCl_4 vapour and also by the author in the spectra of the flames of ($H_2 + CCl_4$), ($H_2 + CHCl_3$), CH_3Cl, C_2H_5Cl and $C_2H_4Cl_2$, but this is not the case.

The methyl iodide flame bands have therefore to be attributed to IO. It is, however, recognised that further additional evidence is necessary before the question is finally decided.

The author wishes to thank Sir C. V. Raman for the excellent facilities provided in his Laboratory for the study of the band-spectra. The author completed this research while working as a Research Student under him before joining the teaching staff of Fergusson College, Poona. The author is also indebted to Dr. P. C. Guha, Head of the Organic Chemistry Department, Indian Institute of Science, and Mr. B. H. Iyer of the Preparation Section of the same Department for the preparation of methyl iodide required during the completion of the research.

Summary.

The spectrum of the flame of methyl iodide burning both with air and oxygen has been found to include a number of bands which do not seem to have been observed before. Tables of their wave-lengths and analysis are given. It has been shown from the analysis that the bands belong to two systems with one electronic level common to them. The emitter of the bands is not definitely known but there are reasons to believe that they may be due to IO.

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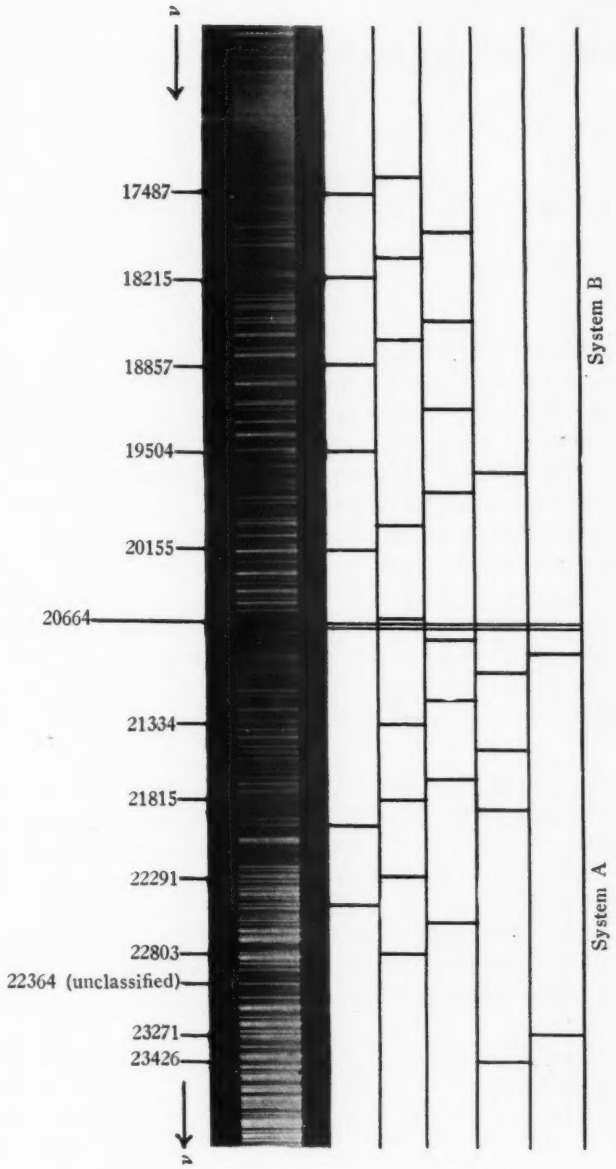
1. Jevons, *Report on Band Spectra of Diatomic Molecules*, 1932, Pp. 234, 281.
2. Sponer, *Molekülspektren*, 1935, *Tabellen* I, p. 85.
3. *Proc. Roy. Soc.*, 1925, 106, 185.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22364 (unclassified)
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ν
System B
System A

RING-SINGULARITY IN BORN'S UNITARY THEORY—II.

By B. S. Madhava Rao.

(University of Mysore.)

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received August 19, 1937.

1. Introduction.

In an earlier paper[1] I have considered a ring-singularity on Born's unitary theory as representing an elementary particle—an electron or a proton. In either case it is possible to obtain finite values for the energy and angular momentum and this is certainly due to the nonlinear character of Born's electrodynamics which solves at one stroke the knotty problem of cohesive forces of non-electromagnetic origin inherent in the old classical theories of structure and inertial mass of the electron. But further results were of a purely negative character. If the model were taken to represent an electron, the ratio of magnetic moment to angular momentum was obtained as $e/2\mu$ and not e/μ, showing that an explanation of the spin was not forthcoming. If the model were taken to represent a proton it was shown possible to derive an estimate of the ring-radius adequate to explain the high mass of the proton, but the ring was not in equilibrium in this position.[2]

Throughout this above investigation, I used a particular form of Born's electrodynamics, *viz.*, the earliest form of Born's field theory.[3] Infeld has shown later[4] that it is possible to find an infinite number of action functions for the new field theory each of which gives simple algebraic relations between the f_{kl} and p_{kl} fields and each leading to a finite energy for an electric particle. Still more recently Hoffmann and Infeld[5] have imposed a regularity condition restricting the choice of the action function and obtained special functions suitable for the cases of special and general relativity.

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[1] B. S. Madhava Rao, *Proc. Ind. Acad. Sci.*, (A), 1936, **4**, 355. This paper will be referred to as I.

[2] See I foot-note on p. 375.

[3] Born and Infeld, *Proc. Roy. Soc.*, (A), 1934, 144, p. 439.

[4] Infeld, *Proc. Camb. Phil. Soc.*, 1935, **32**, 127 ; 1937, **33**, 70.

[5] Hoffmann and Infeld, *Phys. Rev.*, 1937, **51**, p. 765.—Referred to as II.

I have attempted in this paper to carry through my previous investigation on the ring-singularity using the Hoffmann-Infeld action-function in place of Born's action-function. In the considerations of the former action-function the authors restrict themselves to the case where the invariant $G = (\vec{B}\cdot\vec{E})$ does not appear. It may, therefore, appear that this action-function is suitable only for the electrostatic case where $\vec{B} = \vec{H} = 0$. But in my treatment of the ring-singularity I have used the field theory only in the zero-approximation[6] and in this approximation the conditions $(\vec{B}\cdot\vec{E}) = 0$, and $(\vec{D}\cdot\vec{H}) = 0$ are satisfied although $\vec{B}$ and $\vec{H}$ do not vanish.

I use below the same notations as used in my previous paper and indicate only the modifications to be made.

2. Field equations and boundary conditions.

The field equations for axial symmetry and stationary state can be taken over completely from I in the form

$$\left.\begin{aligned} &\frac{\partial H_\rho}{\partial z} - \frac{\partial H_z}{\partial \rho} = \eta v \delta\,; \quad \frac{1}{\rho}\left\{\frac{\partial(\rho D_\rho)}{\partial \rho} + \frac{\partial(\rho D_z)}{\partial z}\right\} = \eta\delta \\ &\frac{\partial(\rho B_\rho)}{\partial \rho} + \frac{\partial(\rho B_z)}{\partial z} = 0\,; \quad \frac{\partial E_z}{\partial \rho} - \frac{\partial E_\rho}{\partial z} = 0 \end{aligned}\right\} \qquad (2,\ 1)$$

The Lagrangian is, however, given by

$$L = H + R$$

the Hamiltonian,[7] by

$$H = \tfrac{1}{2}\log(1 + P) \qquad (2,\ 2)$$

the invariants $F = (\vec{B}^2 - \vec{E}^2)$, $P = (\vec{D}^2 - \vec{H}^2)$, $R = (\vec{B}\,\vec{H}) - (\vec{D}\,\vec{E})$ being connected by the relations

$$R^2 = -F\,P, \text{ and } -(P/F)^{\frac{1}{2}} = 1 + P \qquad (2,\ 3)$$

The boundary conditions at the singularity are given again, as in I, by

$$\left.\begin{aligned} &\int D_\nu ds = \eta\,; \quad \int B_\nu ds = 0 \\ &\int H_s ds = -\eta v\,; \quad \int E_s ds = 0 \end{aligned}\right\} \qquad (2,\ 4)$$

3. Solution in the case of zero-approximation.

Taking $\rho = a$, the equations (2, 1) can be shown, in consonance with the boundary conditions (2, 4), to be satisfied by

$$\left.\begin{aligned} D_\rho &= \frac{\eta}{2\pi r}\cdot\frac{\rho - a}{r} \\ D_z &= \frac{\eta}{2\pi r}\cdot\frac{z}{r} \end{aligned}\right\} \qquad (3,\ 1)$$

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[6] See I—§4, p. 360.

[7] See II—foot-note on p. 768.

$$\left.\begin{aligned} &\text{and,} \quad B_\rho = \lambda E_z, \quad B_z = -\lambda E_\rho \\ &\qquad H_\rho = \lambda D_z, \quad H_z = -\lambda D_\rho \end{aligned}\right\} \tag{3, 2}$$

where $\lambda = v$. Also the above two sets of equations give $(\vec{B}\,\vec{E}) = 0 = (\vec{D}\,\vec{H})$, showing that we can use the Hoffmann-Infeld action-function.

From (3, 1) and (2, 2) we can easily express E_ρ and E_z in terms of D_ρ and D_z. Introducing the absolute field constant b, we can write

$$H = \tfrac{1}{2}\, b^2 \log\left(1 + \frac{\vec{D}^2 - \vec{H}^2}{b^2}\right), \quad \text{and use the relations}$$

$$\vec{E} = \frac{\partial H}{\partial \vec{D}}; \quad \vec{B} = \frac{\partial H}{\partial \vec{H}}. \tag{3, 3}$$

It is perhaps necessary to show that the relations (2, 6) also hold good in the form of the Hoffmann-Infeld theory. But this is very easily deduced from the expressions

$$\left.\begin{aligned} T &= L + H, \\ \text{and,} \quad p^{kl} &= \frac{\partial T}{\partial f_{kl}} \\ f^{*kl} &= \frac{\partial T}{\partial p^*{}_{kl}} \end{aligned}\right\}$$

We can therefore obtain

$$\left.\begin{aligned} E_\rho = \frac{\partial H}{\partial D_\rho} &= \frac{D_\rho}{1 + \frac{a^2}{b^2}(D_\rho{}^2 + D_z{}^2)} \\ E_z = \frac{\partial H}{\partial D_z} &= \frac{D_z}{1 + \frac{a^2}{b^2}(D_\rho{}^2 + D_z{}^2)} \end{aligned}\right\}$$

or, introducing the values of D_ρ and D_z from (3, 1)

$$\left.\begin{aligned} E_\rho &= \frac{\eta}{2\pi} \cdot \frac{\rho - a}{r^2 + r_1{}^2} \\ E_z &= \frac{\eta}{2\pi} \cdot \frac{z}{r^2 + r_1{}^2} \end{aligned}\right\} \tag{3, 4}$$

(3, 2) then immediately leads to

$$\left.\begin{aligned} H_\rho &= \frac{\eta v}{2\pi r} \cdot \frac{z}{r} \\ H_z &= -\frac{\eta v}{2\pi r} \cdot \frac{\rho - a}{r} \end{aligned}\right\} \tag{3, 5}$$

and

$$\left.\begin{aligned} B_\rho &= \frac{\eta v}{2\pi} \cdot \frac{z}{r^2 + r_1^2} \\ B_z &= -\frac{\eta v}{2\pi} \cdot \frac{\rho - a}{r^2 + r_1^2} \end{aligned}\right\} \tag{3, 6}$$

(3, 1), (3, 4)–(3, 6) constitute the field theory solutions in the case of zero-approximation.

4. Calculation of the energy.

We adopt here the same procedure outlined in I, §6 for the calculation of energy and angular momentum and hence there is no need to alter the contributions to these two quantities arising from the classical part. The energy-momentum tensor is given by,[8]

$$T_k^l = \tfrac{1}{2}\{T\delta_k^l + (p^{lm} f_{mk} + f^{*lm} p^*_{mk})\}. \tag{4, 1}$$

This gives

$$T_4^4 = \tfrac{1}{2}\{T + (\vec{D}\,\vec{E}) + (\vec{H}\,\vec{B})\}, \tag{4, 2}$$

The action-function of Hoffmann and Infeld is given by[9]

$$T = \epsilon - \log \epsilon - 1 \tag{4, 3}$$

with $\epsilon = (-F/P)^{\frac{1}{2}}$, so that using (2, 3) we can write (introducing b)

$$T/b^2 = \frac{1}{1+P} + \log(1 + P) - 1.$$

From (3, 1) and (3, 5),

$$P = \frac{1}{b^2}(\vec{D}^2 - \vec{H}^2) = \frac{r_1^2}{r^2}, \text{ and } T \text{ reduces to}$$

$$T = b^2\left\{\log\left(1 + \frac{r_1^2}{r^2}\right) - \frac{r_1^2}{r^2 + r_1^2}\right\}. \tag{4, 4}$$

From (3, 1) and (3, 4),

$$(\vec{D}\,\vec{E}) = \frac{\eta^2}{4\pi^2} \cdot \frac{1}{r^2 + r_1^2} \tag{4, 5}$$

and from (3, 5) and (3, 6),

$$(\vec{B}\,\vec{H}) = \frac{\eta^2 v^2}{4\pi^2} \cdot \frac{1}{r^2 + r_1^2} \tag{4, 6}$$

Substituting from (4, 4), (4, 5) and (4, 6) in (4, 2) the T_4^4-component is given by

$$U_f = T_4^4 = \tfrac{1}{2} b^2\left\{\log\left(1 + \frac{r_1^2}{r^2}\right) - \frac{r_1^2}{r^2 + r_1^2}\right\} + \frac{\eta^2\beta^2}{8\pi^2} \cdot \frac{1}{r^2 + r_1^2}.$$

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[8] See II, p. 769, equation (3, 4).

[9] *Ibid.*, p. 768, equation (1, 20)—There is an obvious misprint here, the minus sign being replaced by a plus sign.

$$E_f = \int U_f \, dV = 4\pi^2 a \int_0^r U_f \, r dr$$

$$= 2\pi^2 ab^2 \int_0^r r \log\left(1 + \frac{r_1^2}{r^2}\right) dr + 2\pi^2 ab^2 r_1^2 \left(\frac{\beta^2}{\alpha^2} - 1\right) \int_0^r \frac{r dr}{r^2 + r_1^2}.$$

$$= 2\pi^2 ab^2 \int_0^r r \log\left(1 + \frac{r_1^2}{r^2}\right) dr + a\eta^2 v^2 \int_0^r \frac{r dr}{r^2 + r_1^2}.$$

$$= \tfrac{1}{2} a\eta^2 a^2 \int_0^x x \log\left(1 + \frac{1}{x^2}\right) dx + \tfrac{1}{2} a\eta^2 v^2 \log(1 + x^2),$$

putting $r = r_1 x$.

$$= \tfrac{1}{2} a\eta^2 a^2 \left\{\tfrac{1}{2} x^2 \log(1 + x^2) + \tfrac{1}{2} \log(1 + x^2) - x^2 \log x\right\} + \tfrac{1}{2} a\eta^2 v^2 \log(1 + x^2)$$

$$= \tfrac{1}{4} a\eta^2 a^2 \left\{x^2 \log\left(\frac{1 + x^2}{x^2}\right)\right\} + \tfrac{1}{4} a\eta^2 \beta^2 \log(1 + x^2) \qquad (4, 7)$$

In the field theory expressions we assume that r is large compared with r_1, *i.e.*, that $x = r/r_1$ is large, and hence the expression within brackets in the first term above is of the order unity, as can be seen from the fact that

$$\operatorname*{Lt}_{x \to 0} x^2 \log\left(1 + \frac{1}{x^2}\right) = \operatorname*{Lt}_{y \to 0} \frac{\log(1 + y^2)}{y^2} = \operatorname*{Lt}_{y \to 0} \frac{2y^2/(1 + y^2)}{2y} = 1.$$

Further a can be neglected since we assume that the velocity v is very nearly equal to the velocity of light, here taken equal to unity. We can, therefore, retain only the second term, wherein we can replace $(1 + x^2)$ by x^2, β by 2, and finally obtain

$$E_f = a\eta^2 \log\left(\frac{r}{r_1}\right) \qquad (4, 8)$$

From equation (7, 4), p. 369 of I,

$$E_{cl} = a\eta^2 \log\left(\frac{8a}{r}\right) \qquad (4, 9)$$

Combining (4, 8) and (4, 9) we get for the total energy

$$E = E_f + E_{cl} = a\eta^2 \log\left(\frac{8a}{r_1}\right) \qquad (4, 10)$$

again a finite value of exactly the same form as in I but only differing from it in having $8a$ in place of $16a$.

5. Calculation of the angular-momentum.

Confining ourselves, as above to the field theory part of the angular-momentum we can write

$$\int M_f \, d\,V = \int \rho(D_z B_\rho - B_z D_\rho) \, dV$$

$$= \frac{\eta^2 v}{4\pi^2} \int\int \frac{\rho \cdot 2\pi \rho d\rho dz}{r^2 + r_1^2}, \quad \text{using (3. 1), (3, 6).}$$

$$= \frac{\eta^2 v}{2\pi} \int_0^r \int_0^{2\pi} \frac{(a + r\cos\phi)^2 \, r dr d\phi}{r^2 + r_1^2}$$

$$= \eta^2 v a^2 \int_0^r \frac{r dr}{r^2 + r_1^2} + \tfrac{1}{2}\eta^2 v \int \frac{r^3 dr}{r^2 + r_1^2}$$

$$= \tfrac{1}{2}\eta^2 v \, (a^2 - \tfrac{1}{2} r_1^2) \log\left(1 + \frac{r^2}{r_1^2}\right) + \tfrac{1}{4}\eta^2 v r^2$$

$$= \eta^2 v a^2 \log\left(\frac{r}{r_1}\right) + \tfrac{1}{4}\eta^2 v r^2, \quad \text{neglecting the term in } r_1^2.$$

From I, p. 372, equation (8, 4)

$$\int M_{cl} \, dV = \eta^2 v a^2 \log\left(\frac{8a}{r}\right) - \tfrac{1}{4}\eta^2 v r^2 \text{ ; therefore}$$

$$M = a^2 \eta^2 \, v \log (8a/r_1) \qquad (5)$$

giving a finite value for the angular-momentum of the same form as in I.

6. Conclusion.

From the expressions for energy and angular-momentum obtained above it is clear that all the considerations of our previous investigation are exactly reproduced. It is practically certain that we will get identical results, if instead of starting with the Hoffmann-Infeld action-function, we start with the several types of action-functions proposed by Infeld. The main purpose of our investigations on the ring-singularity was to test out the possibility of explaining spin classically as suggested by Kramers. In trying to interpret the results of Kramers on the basis of the unitary field theory, Born used the point-singularity model and although it was possible to construct a formal theory there arose contradictions which suggested that point-singularities were not the correct representations of the elementary particles. As a result of the work on the ring-singularity it is now clear that this too does not give a correct representation. The alternative suggests itself that one had better try other types of singularities, but the complications that would be inherent in assuming such higher singularities and the consequent mathematical difficulties almost force us to the conclusion that it is better to go back to the point-singularity and examine its possibilities[10] more thoroughly than has been done so far. It does not appear fruitful to carry further investigations with the ring-singularity.

[10] Prof. Born has kindly informed me by letter that he has examined this question carefully in the course of his lectures to the Poincare Institute, Paris (to be published) and come to the conclusion that point-singularities alone are the correct representations.

STUDIES IN THE FRIEDEL-CRAFTS REACTION.

Part II. The Condensation of the Anhydrides of as-Disubstituted Succinic Acids with Benzene and Toluene.

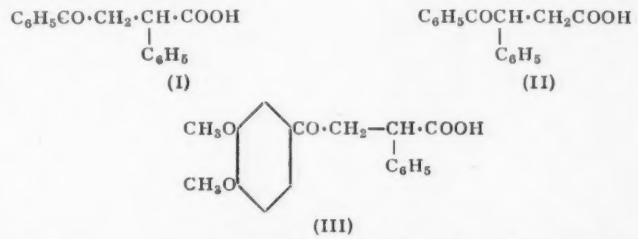
By R. D. Desai and M. A. Wali.

(*From the Department of Chemistry, Muslim University, Aligarh.*)

Received July 12, 1937.

(Communicated by Dr. R. K. Asundi, M.Sc., Ph.D.)

The condensation of the anhydrides of succinic as well as monosubstituted succinic acids with aromatic hydrocarbons in the presence of anhydrous aluminium chloride has been a general method of the synthesis of β-aroylpropionic acids which have been utilised as starting materials for the synthesis of naphthalene as well as phenanthrene derivatives by a number of investigators.[1] In course of certain work connected with the condensation of the anhydrides of various substituted glutaric acids, we happened to repeat the work of Anschütz and co-workers[2] on the condensation of phenyl-succinic anhydride with benzene, and found that it was possible to isolate α-phenyl-β-benzoylpropionic acid (I) together with β-benzoyl-β-phenylpropionic acid (II) which was obtained by them. This work has already been reported in Part I of this series. Robinson and Young[3] found that veratrole condensed with phenylsuccinic anhydride in the presence of aluminium chloride in nitrobenzene solution giving α-phenyl-β-3 : 4-dimethoxybenzoylpropionic acid (III).

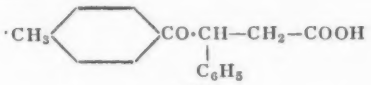


(I) (II)

(III)

We have now condensed toluene with phenylsuccinic anhydride in the presence of aluminium chloride and find that a mixture of β-phenyl-β-*p*-toluoylpropionic (IV) and α-phenyl-β-*p*-toluoylpropionic acids (V) are formed. In the absence of nitrobenzene, (IV) is the main product, while the other isomer preponderated in the presence of nitrobenzene. The structure of α-phenyl-β-*p*-toluoylpropionic acid was proved by its rational synthesis from styryl-*p*-tolyl ketone and hydrogen cyanide according to the method of

Lapworth and Hann.[4] In this connection, it is interesting to observe that Mayer and Stamm[5] have already noticed the formation of a mixture of two acids during the condensation of methylsuccinic anhydride with benzene and toluene.



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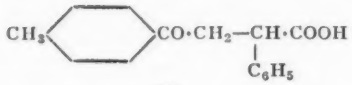
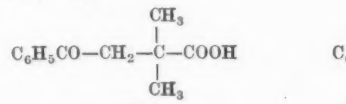


(V)

We thought of extending these observations to the anhydrides of as-disubstituted succinic acids, as the only recorded observation in such a case was the condensation of the anhydride of cyclopentane-1-carboxy-1-acetic acid with benzene by Sen Gupta.[6] The anhydrides of α-α-dimethylsuccinic acid, cyclohexane-1-carboxy-1-acetic acid, and 3-methylcyclopentane-1-carboxy-1-acetic acid were condensed with benzene and toluene in the presence of anhydrous aluminium chloride either in the absence of any solvent or in the presence of nitrobenzene. Under both these conditions α-α-dimethylsuccinic anhydride condensed with benzene giving α-α-dimethyl-β-benzoylpropionic acid (VI) which was easily reduced to α-α-dimethyl-γ-phenylbutyric acid (VII). The acid (VI) reacted with salicylaldehyde in the presence of hydrogen chloride giving a pyrylium salt thus showing the presence of a $-CH_2-CO-$ grouping.[7]

Identical results were obtained with the anhydrides of 3-methylcyclopentane-1-carboxy-1-acetic acid and cyclohexane-1-carboxy-1-acetic acid. Thus benzene and toluene reacted with the former anhydride giving 3-methylcyclopentane-1-carboxy-1-acetophenone (VIII) and 3-methylcyclopentane-1-carboxy-1-*p*-methylacetophenone (IX), while the latter yielded cyclohexane-1-carboxy-1-acetophenone (X) and cyclohexane-1-carboxy-1-*p*-methylacetophenone (XI). All these keto-acids (VIII, IX, X and XI) reacted with salicylaldehyde giving the pyrylium salts while, on reduction, they furnished 3-methylcyclopentane-1-carboxy-1-β-phenylethyl (XII), 3-methyl-cyclopentane-1-carboxy-1-β-*p*-tolylethyl (XIII), and cyclohexane-1-carboxy-1-β-phenylethyl (XIV) respectively.



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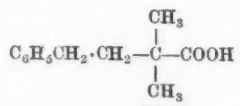

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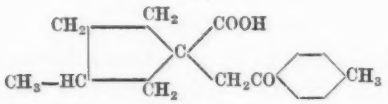

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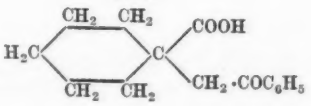

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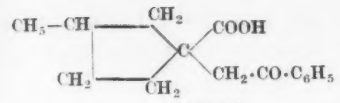

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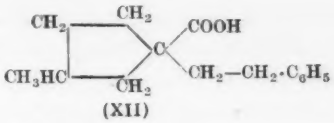

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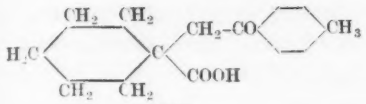

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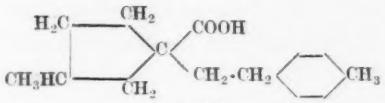
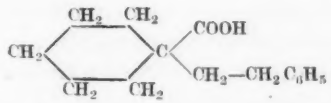
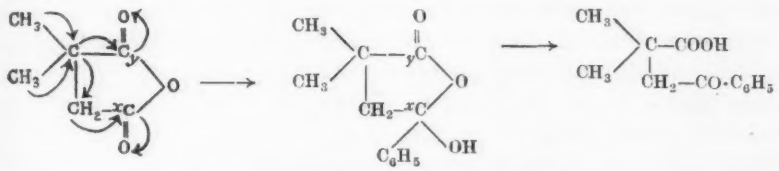


(XIII)



(XIV)

Thus it follows from the above results that the anhydrides of as-disubstituted succinic acids react, either with benzene or toluene, giving only one keto acid, and that only the carbonyl group adjacent to the unsubstituted methylene group is reactive. This can be explained on the electronic conception by assuming that the oxygen of the carbonyl group confers positive charge on the neighbouring carbon by attracting its electrons. The methyl group which is an electron-source gives electrons to the adjacent carbon, and these electrons will be relayed along the chain in both directions, but the carbon of the carbonyl group which is just adjacent to this carbon will receive a greater share than the one which is intercepted by a methylene group. Thus of the two carbons marked *x* and *y*, the former is comparatively more positive than the latter, and therefore, the attachment of the phenyl group (—) and hydrogen (+) will take place as shown below.



This explanation will hold good in the cases of the anhydrides of 3-methylcyclopentane-1-carboxy-1-acetic acid and cyclohexane-1-carboxy-1-acetic acid, but in the case of the phenylsuccinic anhydride a different state of affairs will exist owing to the tautomeric character of the phenyl group. When it behaves as an electron-source, the carbonyl group remote from the substituted methylene group will be reactive, while the reactivity

of the other carbonyl group will be excited when the phenyl group behaves as an electron-sink. This is the reason why a mixture of two isomeric acids is produced in this case.

After this work was over, a paper by Clemo and Dickenson[8] appeared, wherein the condensation of α-α-dimethylsuccinic anhydride with benzene is described and our results corroborate those of the English investigators.

Experimental.

Phenylsuccinic acid was prepared by the condensation of potassium cyanide with benzylidene cyanoacetate according to the method of Lapworth and McRae.[9] The crude condensation product was hydrolysed with concentrated hydrochloric acid, and an almost quantitative yield of the acid m.p. 168° was obtained. The anhydride prepared by heating with an excess of acetic anhydride boiled at 158°/5 mm. and melted at 54° (hexane).

(*A*) *Condensation of Phenylsuccinic anhydride with toluene in presence of anhydrous aluminium chloride and isolation of β-phenyl-β-*p*-toluoylpropionic* (*IV*) *and α-phenyl-β-*p*-toluoylpropionic acids* (*V*).—Powdered aluminium chloride (20 g.) was gradually added to a solution of phenylsuccinic anhydride (10 g.) in dry toluene (30 c.c.) with constant shaking and cooling, and kept at the ordinary temperature for 24 hours. After warming on the water-bath for three hours, the mixture was decomposed with ice-cold dilute HCl and the excess of toluene steam distilled off. The crude acid (10·5 g.) melting at 115–130°, was purified through sodium carbonate solution, and, fractionally crystallised from benzene. The fraction m.p. 148–152°, was recrystallised from methyl alcohol, when white lustrous plates of *β-phenyl-β-*p*-toluoylpropionic acid* m.p. 145° were obtained (5 g.). [Found : C, 76·0 ; H, 6·0 ; $C_{17}H_{15}O_3$ requires C, 76·1 ; H, 5·9 per cent.]

The second fraction obtained from benzene mother liquor melted at 146–148°, and on recrystallisation from methyl alcohol, white cubes m.p. 150°, were obtained. This was the isomeric acid *α-phenyl-β-*p*-toluoylpropionic acid*, as its m.p. was depressed to 130° by admixture with the acid m.p. 154° (yield 3 g.). [Found : C, 75·8 ; H, 6·0 ; $C_{17}H_{15}O_3$ requires C, 76·1 ; H, 5·9 per cent.]

The final fraction from the benzene mother liquor melted at 120–138° (2 g.), and could not be resolved into pure components by any solvent.

Condensation of Phenylsuccinic anhydride with toluene in nitrobenzene solution.—A solution of phenylsuccinic anhydride (5 g.) in dry toluene (15 c.c.) was slowly added with constant shaking and cooling to a solution of aluminium chloride (10 g.) in nitrobenzene (50 c.c.). The mixture was decomposed by dilute HCl after 24 hours, and the nitrobenzene and the

excess of toluene were removed in a current of steam. The crude acid, after being purified by solution in sodium carbonate, was triturated with petroleum ether (b.p. 60–80°) when a white solid (m.p. 115–138°) (5·4 g.) was obtained. Fractional crystallisation through methyl alcohol gave white cubes of *α-phenyl-β-*p*-toluoylpropionic acid*, m.p. 150° (3·5 g.). The second crop of crystals when recrystallised from hexane gave lustrous plates of *β-phenyl-β-*p*-toluoylpropionic acid* (m.p. 154°) (0·6 g.). The final mother liquor gave a fraction m.p. 130–145° (1·3 g.) which frustrated all attempts to purify it through various solvents.

*Synthesis of α-phenyl-β-*p*-toluoylpropionic acid (V) from styryl-*p*-tolyl ketone and potassium cyanide.*—A solution of potassium cyanide (2·5 g.) in water (8 c.c.) was gradually added to a mixture of styryl-*p*-tolyl ketone (3 g.), alcohol (50 c.c.) and glacial acetic acid (1 c.c.). After 24 hours, the alcohol was distilled off, and the resulting gummy product after being washed with water to remove excess of potassium cyanide, was dissolved in concentrated sulphuric acid (15 c.c.). Water was added till permanent turbidity was produced, and the mixture was heated on sand-bath under reflux for 3 hours. The crude acid obtained on cooling the mixture was purified through sodium carbonate solution, and crystallised from methyl alcohol when white cubes (m.p. 150°) were obtained. It did not depress the m.p. of the acid melting at 150°, but lowered the melting point of the acid melting at 154° to 136°.

Attempts to prepare solid *piperonylidene* derivatives of the acids melting at 150° and 154° were not successful. β-phenyl-β-*p*-toluoylpropionic acid was always recovered unchanged after heating with piperonal in alcoholic sodium methoxide solution. When the same reaction was repeated with α-phenyl-β-*p*-toluoylpropionic acid, a gummy, pale-yellow acid was obtained, but no definite solid except piperonylic acid (m.p. 226–227°) was obtained. The failure to recover the original keto-acid suggested that a piperonylidene derivative was perhaps formed.

Recovery of the keto-acid, m.p. 154°, from the fractions, m.p. 120–138° and 130–145° with the help of piperonal.—Piperonal (0·5 g.) and either of the above mixture (0·5 g.) were dissolved in sodium methoxide (0·5 g. Na dissolved in 15 c.c. methyl alcohol), and the mixture kept at the room temperature for 24 hours. The residue left after removing methyl alcohol was dissolved in water, and the filtered solution was acidified with HCl. The semi-solid mass, when crystallised from dilute alcohol gave white plates (m.p. 154°), identical with pure β-phenyl-β-*p*-toluoylpropionic acid. The alcoholic mother liquor left a yellowish gum, and this was possibly the piperonylidene derivative of α-phenyl-β-*p*-toluoylpropionic acid.

Pyrylium derivative of α-phenyl-β-p-toluoylpropionic acid.—A mixture of the keto-acid (0·1 g.) and salicylaldehyde (0·1 g.) in methyl alcohol (10 c.c.) was saturated with hydrogen chloride at 0° C. The mixture, which gradually became deep-red was left overnight and poured into ethyl alcohol containing HCl. The crimson-red precipitate was filtered, washed with alcohol and dried in a vacuum. It was readily soluble in dilute alkali and did not melt upto 290°.

(*B*) *Condensation of the anhydride of cyclohexane-1-carboxy-1-acetic acid with benzene and toluene.*—The anhydride of cyclohexane-1-carboxy-1-acetic acid was prepared according to the directions of Rothstein and Thorpe,[10] and crystallised from hexane in lustrous plates (m.p. 56°).

Isolation of cyclohexane-1-carboxy-1-acetophenone (*X*).—Anhydrous aluminium chloride (10 g.) was gradually added to a solution of the above anhydride (5 g.) in dry benzene (15 c.c.) with constant shaking and cooling. After keeping the mixture at the ordinary temperature for 24 hours, and heating it on the water-bath under reflux for three hours, it was decomposed with cold dilute HCl. The unreacted benzene was removed in steam, and the solid acid obtained on cooling was collected. After purifying it through sodium carbonate solution, the acid crystallised from benzene in white cubes melting at 117° C. (4 g.). [Found : C, 72·9 ; H, 7·1 : $C_{15}H_{18}O_3$ requires C, 73·1 ; H, 7·3 per cent.]

The same keto-acid is obtained by carrying out the reaction in nitrobenzene solution, but the yield is very poor. The keto-acid did not give a solid piperonylidene derivative, and the original acid could never be recovered. The *pyrylium* derivative prepared as usual, was a crimson-red solid, soluble in dilute alkali and not melting upto 290°.

Reduction of cyclohexane-1-carboxy-1-acetophenone and isolation of cyclohexane-1-carboxy-1-β-phenylethyl (*XIV*).—A mixture of the keto-acid (2 g.), zinc amalgam (20 g.) and concentrated HCl (25 c.c.) was heated under reflux for 15 hours after keeping at the ordinary temperature for two hours. The acid obtained on cooling crystallised from petroleum ether in white needles melting at 90°. [Found : C, 77·5 ; H, 8·6 ; $C_{15}H_{20}O_2$ requires C, 77·6 ; H, 8·6 per cent.]

Condensation of the anhydride with toluene and isolation of cyclohexane-1-carboxy-1-p-methylacetophenone (*XI*).—Powdered aluminium chloride (10 g.) was gradually added to a solution of the anhydride (5 g.), with constant shaking and cooling in dry toluene (15 c.c.). After allowing the mixture to stand at the ordinary temperature for 24 hours, it was heated on the water-bath for three hours, and decomposed with cold, dilute HCl. When

the solution was cooled after the removal of toluene in steam, the solid acid which was precipitated was collected and purified through sodium carbonate solution. It melted at 122–128°, but on recrystallisation from methyl alcohol rectangular plates melting at 130° were obtained (yield 6·6 g.). [Found : C, 73·6 ; H, 7·6 ; $C_{16}H_{20}O_3$ requires C, 73·8 ; H, 7·7 per cent.]

The acid failed to give a solid piperonylidene derivative. The *pyrylium* derivative, which was a crimson-red powder, was soluble in dilute sodium hydroxide and did not melt upto 290°.

Condensation of the anhydride with toluene in nitrobenzene solution and isolation of cyclohexane-1-p-*toluoyl*-1-p-*methylacetophenone*.—The condensation was carried out as usual using the anhydride (5 g.), dry toluene (15 c.c.), nitrobenzene (50 c.c.) and aluminium chloride (10 g.). The resulting crude solid left after the removal of nitrobenzene and toluene in the steam melted at 108–118° (yield 6·6 g.). On treating with sodium carbonate solution, the insoluble portion (2 g.) melted at 132–135°, and on recrystallisation from methyl alcohol white, thick, prismatic needles melting at 138° were obtained. The substance is insoluble in dilute sodium hydroxide. [Found : C, 82·2 ; H, 7·8 ; $C_{23}H_{26}O_2$ requires C, 82·6 ; H, 7·8 per cent.]

The diketone did not give a solid piperonylidene derivative. The *pyrylium derivative* was a deep vermilion coloured powder insoluble in dilute alkali and not melting below 290°.

The sodium carbonate solution, on acidification gave, an acid melting at 130° identical with cyclohexane-1-carboxy-1-*p*-methylacetophenone.

(*C*) *Condensation of the anhydride of* 3-*methylcyclopentane*-1-*carboxy*-1-*acetic acid with benzene and isolation of* 3-*methylcyclopentane*-1-*carboxy*-1-*acetophenone* (*VIII*).—The anhydride (10 g.) prepared by the method of Desai,[11] and benzene (30 c.c.) were condensed as usual in presence of aluminium chloride (18 g.). *The acid*, purified through sodium carbonate melted at 125–135°, but on recrystallisation from benzene-hexane mixture, white, silky needles melting at 147° were obtained (yield 8·5 g.). The same acid was obtained in a poor yield by carrying out the condensation in presence of nitrobenzene. [Found : C, 73·1 ; H, 7·2 : $C_{15}H_{18}P_3$ required C, 73·1 ; H, 7·3 per cent.]

It did not give a solid piperonylidene derivative, and its *pyrylium derivative* was a crimson-red powder soluble in dilute alkali and not melting upto 290°.

3-*Methylcyclopentane*-1-*carboxy*-1-*β*-*phenylethyl* (*XII*) was prepared by reducing the keto-acid with amalgamated zinc as usual. The crude solid

(m.p. 56–67°) was obtained in white needles (m.p. 70°) after several crystallisations from petroleum ether. [Found : C, 77·5 ; H, 8·5 ; $C_{15}H_{20}O_2$ requires C, 77·5 ; H, 8·6 per cent.]

Condensation with toluene and isolation of 3-*methyl-cyclopentane*-1-*carboxy*-1-p-*methylacetophenone* (*IX*).—The proportions used were toluene (15 c.c.), the anhydride (5 g.) and aluminium chloride (9 g.). The solid purified through solution in sodium carbonate solution melted at 120–132°, but recrystallisation from methyl alcohol gave thick, white plates m.p. 144° C. (yield 6·0 g.). [Found : C, 73·7 ; H, 7·9 ; $C_{16}H_{20}O_3$ requires C, 73·2 ; H, 7·9 per cent.]

The *same acid* was exclusively obtained by carrying out the condensation in presence of nitrobenzene, and the yield was very good. The *piperonylidene derivative* was a pale yellow gum, while the *pyrylium derivative* was a crimson-red powder, soluble in dilute alkali and unmelted below 290° C.

3-*Methylcyclopentane*-1-*carboxy*-1-β-p-*tolylethyl* (*XIII*) was obtained by reducing the keto-acid with zinc amalgam as usual. The crude acid (m.p. 40–50°), crystallised from hexane in white cubes melting at 62° C. [Found : C, 77·4 ; H, 8·7 ; $C_{16}H_{22}O_2$ requires C, 77·6 ; H, 8·6 per cent.]

(*D*) *Condensation of the anhydride of* α-α-*dimethylsuccinic acid with benzene, and isolation of* α-α-*dimethyl*-β-*benzoylpropionic acid* (*VI*).—α-α-Dimethylsuccinic anhydride (10 g.) (Higson and Thorpe[12]) was condensed with dry benzene (30 c.c.) in presence of aluminium chloride (18 g.) as usual. The crude acid, after usual purification, melted at 166–168°, and on recrystallisation from benzene, long silky needles melting at 172–173°, were obtained (yield 15 g.). [Found : C, 70·2 ; H, 6·9 ; $C_{12}H_{14}O_3$ requires C, 69·8 ; H, 6·7 per cent.]

The piperonylidene derivative was a yellowish gum which did not give any crystalline solid. The *pyrylium derivative* was a crimson-red powder, soluble in dilute caustic soda, and not melting below 290° C.

α-α-*Dimethyl*-γ-*phenylbutyric acid* (*VII*) was obtained by reducing the keto-acid with amalgamated zinc as usual. It crystallised from petroleum ether in needles melting at 96° C. [Found : C, 75·1 ; H, 8·3 : $C_{12}H_{16}O_2$ requires C, 75·0 ; H, 8·3 per cent.]

We have great pleasure in recording our thanks to Dr. R. F. Hunter for his kind interest in this work.

Summary of Part II.

The anhydride of phenylsuccinic acid has been found to give two isomeric keto-acids on condensing with toluene in the presence of anhydrous

aluminium chloride. On extending this observation to the anhydrides of α-α-dimethylsuccinic acid, 3-methylcyclopentane-1-carboxy-1-acetic acid and cyclohexane-1-carboxy-1-acetic acid, it was found that each of them gave only one keto-acid on condensing with benzene and toluene. An explanation has been offered on the electronic conception.

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N. B.— The paper by Ahmad Ali, Desai, Hunter and Muhammad (*J.*, 1937, 1013) forms Part I of this series.

STUDIES IN THE FRIEDEL-CRAFTS REACTION.

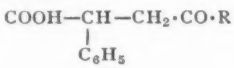
Part III. The Condensation of Succinic Anhydride with the Methyl Ethers of the Phenol and the Cresols.

R. D. DESAI AND M. A. WALI.

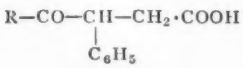
(From the Department of Chemistry, Muslim University, Aligarh.)

Received July 12, 1937.

WE have already described the condensation of phenylsuccinic anhydride with benzene and toluene with the result that two isomeric acids represented by formulæ I and II (where R = phenyl or *p*-tolyl) are always produced (see preceding paper). While extending this observation to anisole, we observed that complications arose owing to the condensation of anisole either in the *ortho* or *para* position to the methoxy group. In order to make sure of the position taken up in the benzene ring, we decided to repeat the observations of Rosenmund and Schapiro[1] on the condensation of succinic anhydride with the methyl ethers of the phenol, and the three isomeric cresols.

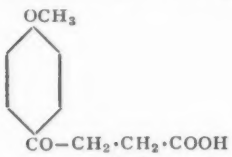


(I)



(II)

Succinic anhydride condensed with anisole, either in nitrobenzene or acetylene tetrachloride solution, giving β-(4-methoxy-benzoyl)-propionic acid (III) together with a small quantity of a phenolic product which was identified as α-β-4 : 4'-dihydroxydibenzoylethane (IV), because it was oxidised by alkaline hypobromite to *p*-hydroxybenzoic acid and ethylenedibromide. The constitution of the acid (III) followed from the fact that oxidation with alkaline hypobromite gave *p*-methoxybenzoic acid. The Clemmensen reduction of this keto-acid gave γ-4-methoxyphenylbutyric acid.



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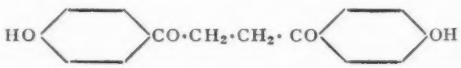
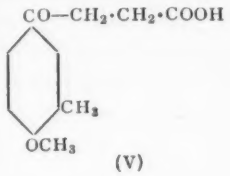


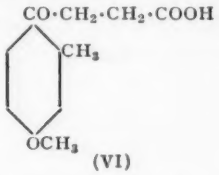
(IV)

Methyl-*o*-cresyl ether gave β-(3-methyl-4-methoxy-1-benzoyl)-propionic acid (V) as it was oxidised to 3-methyl-4-methoxybenzoic acid. The keto-acid was reduced to γ-(3-methyl-4-methoxyphenyl)-butyric acid. Methyl-*m*-cresyl ether yielded β-(2-methyl-4-methoxy-1-benzoyl)-propionic acid (VI),

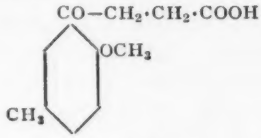
as it gave, on oxidation, 2-methyl-4-methoxybenzoic acid. Finally, methyl-*p*-cresyl ether gave β-(2-methoxy-5-methyl-1-benzoyl)-propionic acid (VII), as it was oxidised to 2-methoxy-5-methylbenzoic acid.



(V)



(VI)



(VII)

Experimental.

Condensation of succinic anhydride with anisole and isolation of β-(4-methoxy-1-benzoyl)-propionic acid (III) and α-β-4-4'-dihydroxydibenzoyl ethane (IV).—Succinic anhydride (14·5 g.) was dissolved in a well-cooled solution of aluminium chloride (40 g.) in nitrobenzene (150 c.c.). Anisole (15 g.) was gradually added with constant stirring and cooling, and the mixture was allowed to stand at the ordinary temperature for 48 hours. After decomposing the mixture with dilute HCl, the unreacted anisole and nitrobenzene were removed in steam, and the solid obtained on cooling the solution was collected. On treatment with sodium carbonate solution, a portion of the solid remained undissolved (4 g.). The alkaline solution, on acidification with concentrated HCl, gave an *acid* melting at 138–146° (10 g.). On recrystallisation from methyl alcohol, short, prismatic needles melting at 148°, were obtained (Rosenmund gives 146°). [Found : C, 63·3 ; H, 5·8 ; $C_{11}H_{12}O_4$ requires C, 63·4 ; H, 5·7 per cent.]

Oxidation of the keto-acid, m.p. 148°, to 4-methoxybenzoic acid.—The stock solution of sodium hypobromite was prepared by adding bromine (32 c.c.) to the cooled solution of caustic soda (26 g.) in water (100 c.c.). For the purpose of oxidation, 3 c.c. of this solution diluted to 50 c.c., were used for 0·5 g. of the acid.

Sodium hypobromite solution (3 c.c. diluted to 50 c.c.) was gradually added to a well-cooled soultion of the keto-acid (0·5 g.) dissolved in caustic soda. After keeping the mixture for 24 hours at the ordinary temperature, the excess of the hypobromite was removed by sulphur dioxide, and the alkaline solution acidified with concentrated HCl. The precipitated acid on recrystallisation from alcohol melted at 183°–184°, and was identified as 4-methoxybenzoic acid, by comparison with an authentic specimen.

The portion insoluble in sodium carbonate dissolved in 10 per cent. caustic soda solution, and a white solid melting at 40–46° was obtained on acidification with dilute HCl. Recrystallisation from hexane gave white

silky needles melting at 54°. [Found : C, 66·4 ; H, 5·8, $C_{16}H_{14}O_4H_2O$ requires C, 66·6 ; H, 5·5 per cent.]

Oxidation with sodium hypobromite.—The diketone (0·5 g.) dissolved in caustic soda solution was oxidised by the hypobromite (3 c.c.) as described above. The neutral product was extracted with ether, the alkaline solution was acidified with strong HCl and the resulting solid crystallised from alcohol. It melted at 209–210° and was identified as *p*-hydroxybenzoic acid by comparison with an authentic specimen.

γ-(4-methoxyphenyl)-butyric acid.—A mixture of the keto-acid (2 g.) amalgamated zinc (20 g.) and concentrated HCl (25 c.c.) was heated under reflux on sand-bath for 12 hours. The resulting semi-solid acid was purified through solution in sodium carbonate, and crystallised from hexane when short, white needles melting at 62° were obtained. [Found : C, 67·9 ; H, 7·2 : $C_{10}H_{14}O_3$ requires C, 68·0 ; H, 7·2 per cent.]

Condensation of succinic anhydride with o-*cresol methyl ether.*—This was carried out as usual using succinic anhydride (4 g.), *o*-cresyl methyl ether (5 g.), nitrobenzene (60 c.c.) and aluminium chloride (12 g.), and giving 60 hours for the reaction to complete. After the usual purification, *β-(4-methoxy-3-methyl-1-benzoyl)-propionic acid* crystallised from benzene in long white needles melting at 150° (Rosenmund gives 146°). When the keto-acid was oxidised by means of sodium hypobromite as usual, 3-methyl-4-methoxybenzoic acid[2] (m.p. 191–192°) was produced.

Reduction by amalgamated zinc gave *γ-(3-methyl-4-methoxyphenyl)-butyric acid* which crystallised from benzene in white, fine needles melting at 98–99°. [Found : C, 68·9 ; H, 7·4 ; $C_{12}H_{16}O_3$ requires C, 69·2 ; H, 7·7 per cent.]

The condensation of succinic anhydride with m-*cresyl methyl* ether gave *β-(2-methyl-4-methoxy-1-benzoyl)-propionic acid* ; as it was oxidised by alkaline hypobromite to 2-methyl-4-methoxybenzoic acid[2] (m.p. 175–176°).

Reduction by the usual method gave *γ-(2-methyl-4-methoxyphenyl)-butyric acid* which crystallised from hexane in white, lustrous plates melting at 92°. [Found : C, 69·2 ; H, 7·6 ; $C_{12}H_{16}O_3$ requires C, 69·2 ; H, 7·7 per cent.].

p-*Cresyl methyl* ether and succinic anhydride gave *β-(5-methyl-2-methoxy-1-benzoyl)-propionic acid*, as it was oxidised by alkaline sodium hypobromite to 5-methyl-2-methoxybenzoic acid[2] (m.p. 70°).

Reduction of the keto-acid by the usual method gave *γ-(5-methyl-2-methoxyphenyl)-butyric acid* which crystallised from hexane in white needles, melting at 66°. [Found : C, 69·2 ; H, 7·7 : $C_{12}H_{16}O_3$ requires C, 69·2 ; H, 7·7 per cent.]

We have great pleasure in expressing our thanks to Dr. R. F. Hunter for his kind interest in this investigation.

Summary of Part III.

The condensation of anisole with succinic anhydride gave β-(4-methoxybenzoyl)-propionic acid, and a small quantity of α-β-4 : 4'-dihydroxydibenzoylethane.

Similar condensation has been carried out with the methyl ethers of the three cresols. The constitution of these various keto-acids has been determined by oxidation. They have been also reduced to the corresponding substituted butyric acids.

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GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

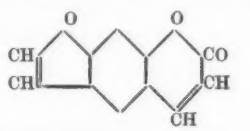
Part V. The Behaviour of Psoralic and Isopsoralic Acids.

By P. Suryaprakasa Rao, C. Venkata Rao
and
T. R. Seshadri.

(*From the Department of Chemistry and Technology, Andhra University, Waltair.*)

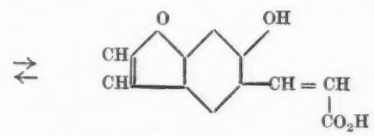
Received August 12, 1937.

The early attempts of Karrer, Glattfelder and Widmer[1] to prepare members of the Bergapten group starting from hydroxycoumarones ended in failure. As a possible explanation for this it was suggested (Ray *et al.*[2]) that the intermediate hydroxycoumarone acrylic acids produced in their experiments had the *trans*-configuration and hence did not undergo ring closure. This led us to examine some *trans* acids of this series with reference to their capacity to undergo geometrical inversion and ring closure. Two of this group can be easily made from Psoralen (I) and Isopsoralen (II) which have been recently obtained from the seeds of *Psoralia Corylifolia*.[3,4,5] The *cis* acids from these two substances are unstable and are formed only in alkaline solutions. They are now named Psoralinic and Isopsoralinic acids. Their methyl ethers are, however, stable and have been prepared by Jois and Manjunath[4] by methylating the alkaline solutions. The stable *trans* acids have not hitherto been made, though their ethers were obtained by the above authors by the sublimation of the *cis* acid ethers *in vacuo*. These *trans* acids have now been obtained by the method of Seshadri and Rao using cold mercuric oxide and caustic soda.[6] They are named Psoralic (III) and Isopsoralic acids (IV). They are stable and they confirm to the behaviour of stable *trans* acids in all their reactions. They have been converted into their methyl ethers which were originally obtained from the *cis* compounds by sublimation *in vacuo*.[4]



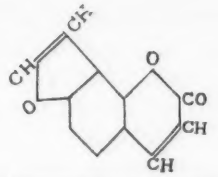
Psoralen (coumarono-6 : 5-α-pyrone).

I



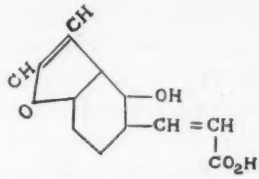
Psoralic acid (6-hydroxycoumarone-5-acrylic acid).

III



Isopsoralen (coumarono-4 : 5-α-pyrone).

II



Isopsoralic acid (4-hydroxycoumarone-5-acrylic acid).

IV

Psoralic and Isopsoralic acids are isomeric and offer scope for studying the influence of structure on the facility with which ring closure to the pyrone can take place. As will be noticed the first acid will give rise to a linear and the second to an angular compound and in general it is known that the formation of an angular ring compound is favoured (see Rangaswami and Seshadri[7]). In the ring formation from the above two acids there are two factors that are involved : (1) the facility with which *trans* to *cis* inversion takes place and (2) the ease with which ring closure with the elimination of water takes place.

In the presence of concentrated sulphuric acid the above hydroxy-coumarone-acrylic acids were unstable and were rapidly converted into dark resinous products from which no crystalline substance could be isolated. On the other hand they underwent smooth conversion into the corresponding coumarono-α-pyrones in the presence of sunlight. By comparative experiments it was found that the change was more ready in the case of Isopsoralic acid (75 per cent. in 16 hours) than with Psoralic acid (58 per cent.). When aqueous mercuric chloride was employed there was some resinification so that no comparisons could be correctly made though in this case also Isopsoralic acid gave a better yield of the pyrone (50 per cent.) than Psoralic acid (25 per cent.). To which of the two factors that have been mentioned in the previous paragraph this difference should be attributed is difficult to decide.

In the examples studied in this paper, though the angular compound appears to be more readily formed than the linear variety, still the difference is not great when comparison is made with the formation of fresh rings starting from only one group like the OH or NH_2. In these cases the angular compound is either the sole product or is predominantly the major product. This seems to be obviously due to the reactivity of the alternative nuclear positions one of which is preferentially favoured.

Experimental.

The best method of isolating the crude mixture of Psoralen and Isopsoralen from the seeds of *Psoralia Corylifolia* has already been described.[5] It melted at about 110°–115°. The separation of the two was

effected as follows :—5 grams of the mixture was dissolved in a fair excess of boiling ethyl alcohol, filtered from any suspended impurities and allowed to cool slowly. Colourless, large and hard crystals (rhombohedral plates and prisms) were obtained in the course of two hours. The mixture was then stirred, filtered and the crystals washed with a small quantity of alcohol. The solid now melted at 156°–58° with a little previous sintering. A further crystallisation from aqueous alcohol raised the melting point to 167°–68° (Jois *et al.* 162° ; Spath *et al.* 171°). This had all the properties of Psoralen as described by Jois *et al.*[3] (yield 2·2 g.).

The alcoholic mother liquor on concentration to half its bulk and cooling gave a crop of soft fine needles melting at 128°–32°. Two further crystallisations from dilute alcohol raised the melting point to 141°–42° (Jois and Manjunath[4] gave for Isopsoralen 142° and Spath and Pesta gave for Angelicin 139°).[8] This compound agreed with previous descriptions of Isopsoralen and Angelicin (yield 0·8 g.).

The residual alcoholic mother liquor on further concentration and treatment with water gave a large crop of a crystalline solid melting at 118°–20°. Repeated crystallisation from alcohol did not produce any change and the melting point was fairly sharp. Analysis however, showed that it had the same composition as Psoralen or Isopsoralen and was obviously a mixture of the two having the characteristic of a fairly sharp melting point [Found : C, 70·9, H 3·4 ; $C_{11}H_6O_3$ requires C, 71·0, H, 3·2%]. It was therefore dissolved in chloroform in which it was readily soluble and treated with ether till precipitation just occurred. The precipitated solid was collected after twelve hours and was found to be mostly Psoralen which could now be rendered pure by two crystallisations from dilute alcohol. The chloroform ether solution gave a solid on evaporation from which small quantities of Isopsoralen could be isolated by repeated crystallisation from aqueous alcohol. Fractional crystallisations using carbon tetrachloride or pyridine were also found to be effective. Psoralen was comparatively easily obtained from the more sparingly soluble portions whereas the separation of Isopsoralen was far more difficult and tedious.

Preparation of Psoralic acid.—Psoralen (1 g.) was dissolved in hot 5% aqueous sodium hydroxide (20 c.c.), the solution cooled to room temperature, treated with yellow mercuric oxide (0·5 g.) and shaken vigorously for about 15 minutes. The mixture was then filtered through an ordinary filter and the residue washed with a little water. The filtrate was then saturated with hydrogen sulphide and after mercury had been completely precipitated, it was filtered and washed with small quantities of water. On strongly acidifying the filtrate Psoralic acid was obtained, as a crystalline

solid melting at about 220° with decomposition. It was easily crystallised from aqueous alcohol as rectangular prisms melting with decomposition at 225°–27° [Found : C, 64·2 ; H, 4·0 ; $C_{11}H_8O_4$ requires C, 64·7 ; H, 3·9%]. It was noticed that during the shaking with mercuric oxide considerable mercuration occurred. If the combined mercury was not removed as described above the precipitated acid melted at about 195°. The yield under the best conditions was 90%. Care had to be taken that no rise of temperature was allowed to take place during the course of the preparation and during acidification. Cooling with ice was employed.

Methyl ether of Psoralic acid.—Psoralic acid (0·4 g.) was dissolved in a mixture of methyl alcohol (6 c.c.) and 20% sodium hydroxide (10 c.c.). After raising the temperature to 80°, the solution was agitated vigorously and methyl sulphate (2 c.c.) was added. The mixture turned milky on shaking. It was then heated on a water-bath at 80° for 5 minutes, treated with 6 c.c. more of the alkali and heated for 5 minutes more with vigorous agitation. Methyl sulphate (2 c.c.) and alkali (6 c.c.) were now added alternately with shaking and heating between the additions till the methyl sulphate introduced amounted to 8 c.c. Finally 6 c.c. of methyl sulphate and 12 c.c. of alkali were added and the mixture refluxed on a steam-bath for 30 minutes longer. The contents were cooled, filtered and acidified. The crude methyl ether was obtained in a yield of 90%. It is easily soluble in alcohol, acetic acid and pyridine and was crystallised from aqueous pyridine as rhombic prisms melting at 223°–24°. Jois and Manjunath who obtained this ether by sublimation *in vacuo* of the ether of the *cis* acid give the melting point as 234°–5° [Found : C, 66·5 ; H, 4·8 ; $C_{12}H_{10}O_4$ requires C, 66·1 ; H, 4·6%].

Isopsoralic acid.—This acid was obtained from Isopsoralen by closely following the method used for Psoralic acid and a similar high yield was obtained. It came down as colourless rectangular tablets from dilute alcohol and melted at 173°–75° with decomposition [Found : C, 64·5, H, 4·2 ; $C_{11}H_8O_4$ requires C, 64·7 ; H, 3·9%].

The *Methyl ether* of Isopsoralic acid was obtained by methylation as described already. It crystallised from dilute pyridine in rhombic plates melting at 213°–14°. Jois and Manjunath gave the melting point of the sample obtained by the sublimation of the *cis* compound as 214° [Found : C, 65·6 ; H, 4·9 ; $C_{12}H_{10}O_4$ requires C, 66·1 and H, 4·6%].

Conversion of the trans *acids into the pyrones.*—(i) In the presence of concentrated sulphuric acid the acids underwent complex decomposition and were rapidly converted into dark resinous products from which no definite compound could be isolated.

(ii) *Exposure to sunlight.*—The acid (about 1 g.) was weighed correctly and dissolved in anhydrous ethyl alcohol (50 c.c.) contained in a quartz round bottom flask of capacity 100 c.c. The solution was then exposed to direct sunlight for 16 hours (2 days of 8 hours—8 A.M. to 4 P.M.). The solvent was distilled off and the residue taken up in a mixture of chloroform and ether. This solution was extracted with 5% aqueous sodium carbonate till no more acid was removed and the correct stage could be ascertained from the colour of the aqueous extract. Two extractions were usually found to be sufficient. The chloroform-ether was washed with a small quantity of water, dried over calcium chloride and finally distilled in a tared conical flask to remove the solvent. The residue after being dried in a vacuum desiccator was weighed. This consisted of the coumaronopyrone (furanocoumarin) as could be ascertained from its melting point. From the aqueous sodium carbonate extract the acid could be recovered by acidification and filtration. Psoralic acid gave 58% yield of Psoralen whereas Isopsoralic acid gave 75% yield of Isopsoralen.

(iii) *Boiling with aqueous mercuric chloride.*—Psoralic acid (1 g.) was treated with water (100 c.c.) and mercuric chloride (0·5 g.) and the mixture boiled for 3 hours. A good amount of an amorphous solid was formed. Concentrated hydrochloric acid (4 c.c.) was added to the hot solution and then allowed to cool slowly. The solid matter was then filtered and dissolved in a mixture of chloroform and ether. A fair amount of a complex resinous matter was left behind and no crystalline compound could be obtained from it. The chloroform-ether solution was then extracted repeatedly with aqueous sodium bicarbonate in order to remove unconverted acid, washed with water and subsequently with dilute hydrochloric acid and then evaporated in a tared flask. Pure Psoralen was then obtained in a yield of 25%.

Starting with Isopsoralic acid the conversion was carried out in the same way. There was very little of resin formation and the yield of Isopsoralen was 50%.

Summary.

The stable *trans* acids, Psoralic and Isopsoralic acids, have been prepared from Psoralen and Isopsoralen. With concentrated sulphuric acid they undergo complex changes whereas in the presence of sunlight and aqueous mercuric chloride they yield the original pyrones. Though Isopsoralic acid undergoes ring closure more easily the difference is not great.

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6. T. R. Seshadri and P. Suryaprakasa Rao, *ibid.*, 1936, **4**, 293.
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ADDENDUM.

"A Practical Financial Transaction."

By G. S. Diwan and V. V. Narlikar.*

We wish to refer here to Dr. Steffenon's paper, quoted by us in our paper *supra* and particularly to Mr. C. G. Lidstone's remarks on that paper published in the same number.†

Dr. Steffenson says, "We propose to show that if the value of all outstanding payments at any given time, A's payments reckoned positive and B's negative, does not change its sign, then there is not more than one possible rate of interest." Here as well as in the proof given later he assumes that this constancy of the sign holds good on the basis of *any positive rate of interest whatsoever*; whereas in our note we have assumed that this constancy of the sign holds good on the basis of *some particular positive rate of interest.*

Mr. Lidstone's demonstration based on general considerations is extremely interesting and instructive. It is worth noting that when his general considerations are translated into mathematical symbols, they give probably the simplest proof of the special problem of our note, inasmuch as the proof is then reduced to the identity

$$a_0 (a+h)^n + a_1 (a+h)^{n-1} + \ldots + a_{n-1} (a+h) + a_n = [a_0 a^n + a_1 a^{n-1} + \ldots$$
$$\ldots + a_{n-1} a + a_n] + a_0 h (a+h)^{n-1} + (a_0 a + a_1) h (a+h)^{n-2} + \ldots$$
$$\ldots + (a_0 a^{n-1} + a_1 a^{n-2} + \ldots + a_{n-1}) h; \quad (a+h)$$

being what we have called β in our note and $1 + i + h$ in terms of Lidstone's notation.

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* *Proc. Ind. Acad. Sci.*, 1935, **II**, No. 2, Sec. A.

† *J. Inst. Actu.*, **64**, 169-171.